ELECTRONIC STRUCTURE IN FIVE-COORDINATE COMPLEXES OF NICKEL(II) WITH HEAVY-DONOR LIGANDS

Thesis by

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To Jean

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ABSTRACT

I.

Various studies designed to elucidate the electronic structure of the arsenic donor ligand, o-phenylenebisdimethylarsine (diarsine), have been carried out. The electronic spectrum of diarsine has been measured at 300 and 77°K. Electronic spectra of the molecular complexes of various substituted organoarsines and phosphines with tetracyanoethylene have been measured and used to estimate the relative ionization potentials of these molecules.

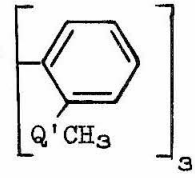
Uv photolysis of arsines in frozen solution (96°K) has yielded thermally labile, paramagnetic products. These include the molecular cations of the photolyzed compounds. The species $(diars)^+$ exhibits hyperfine splitting due to two equivalent $^{75}As(I=3/2)$ nuclei. Resonances due to secondary products are reported and assignments discussed.

Evidence is presented for the involvement of d-orbitals in the bonding of arsines. In $(diars)^+$ there is mixing of arsenic "lone-pair" orbitals with benzene ring π-orbitals.

II.

Detailed electronic spectral measurements at 300 and 77°K have been carried out on five-coordinate complexes of low-spin nickel(II), including complexes of both trigonal bipyramidal (TBP) and square pyra-

midal (SPY) geometry. TBP complexes are of the form $NiLX^+$ (X=halide or cyanide,

$L = Q[(CH_2)_3As(CH_3)_2]_3$ or P  , Q = P, As,

Q'=S,Se).

The electronic spectra of these compounds exhibit a novel feature at low temperature. The first ligand field band, which is asymmetric in the room temperature solution spectrum, is considerably more symmetrical at 77°K. This effect is interpreted in terms of changes in the structure of the complex.

The SPY complexes are of the form $Ni(diars)_2X^Z$ (X=Cl,Br,I,CNS,CN, thiourea,NO_2,As). On the basis of the spectral results, the d-level ordering is concluded to be $xy < xz,yz < z^2 \ll x^2 - y^2$. Central to this interpretation is identification of the symmetry-allowed $^1A_1 \rightarrow {}^1E$ ($xz,yz \rightarrow x^2 - y^2$) transition. This assignment was facilitated by the low temperature measurements.

An assignment of the charge-transfer spectra of the five-coordinate complexes is reported, and electronic spectral criteria for distinguishing the two limiting geometries are discussed.

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ELECTRONIC STRUCTURE OF SUBSTITUTED ARSINES

CHAPTER 1

INTRODUCTION--THE NATURE OF PHOSPHINES AND ARSINES AND THEIR TRANSITION-METAL COMPLEXES

Stable complexes of transition metal ions with ligands containing the heavy donor atoms arsenic and phosphorus have been known for many years (1). More recently, extensive synthetic work has been carried out in these systems, and complexes of either phosphines or arsines are known with nearly all the transition metals (2).

The behavior of arsenic and phosphorus donor ligands towards metal ions is rather different from that of the corresponding nitrogen donor ligands. In particular, while the tertiary amine ligands exhibit so-called "hard" base or "Class a" behavior, arsines and phosphines consistently behave as "soft" bases, or "Class b" electron donors (3,4). Arsenic and phosphorus donor ligands tend to stabilize four- and five-coordinate complexes, particularly in the d^8 systems studied here, while complexes of nitrogen donor ligands are generally six-coordinate, in the absence of severe steric factors (5). Also, arsine and phosphine complexes tend to be low-spin, and amine complexes high spin (2).

As is generally true, the stability of phosphine and arsine complexes increases dramatically when monodentate ligands are replaced with polydentate ligands. However, while polydentate primary and secondary amine ligands readily ionize to form stable conjugated chelate systems with metal ions (e.g., di-imines and Schiff's base derivatives), the corresponding phosphine and arsine complexes have not been made,

presumably as a result of the aversion of second- and third-row elements to multiple bonding, particularly with first-row elements (6). It is also true that polydentate primary and secondary phosphines and arsines are exceedingly rare, presumably because of the necessity to have alkyl or aryl groups present for stability.

Phosphines exhibit a strong trans-labilizing effect in the square planar complexes of platinum(II); amines are not trans-labilizing (7). The extinction coefficients observed in the ligand field portion of electronic absorption spectra are much higher in arsine and phosphine complexes than in amine complexes, by a factor of anywhere from ten to one thousand (8,9). Concerning the ligand field strengths of ligands involving N, P, and As donor atoms, not much data are available. Chatt et al. (10) report the spectrochemical series ordering $P \gtrsim N \gtrsim As$ for trans-PtL(piperidine) X_2 complexes. They point out that the ordering is very likely sensitive to the nature of the metal ion, the relative ligand field strength of N increasing with increasing oxidation state of the metal.

Much of the above description of properties is applicable to a comparison of complexes of oxygen donor ligands with those of sulfur- and selenium-donors. It is of course true that many stable and interesting sulfur-donor chelates have been prepared using bidentate, anionic sulfur ligands (11). Also, it appears that the spectrochemical series ordering for these donor atoms proceeds regularly down the column, $O > S > Se > Te$ (10,11).

Pearson (4) has summarized the various factors contributing to hard vs. soft acid or base behavior. It appears that these factors are

important in the differences in behavior between the first-row donor (N,O) complexes and the heavy donor (P,As,S,Se) complexes. These factors are (1) ionic vs. covalent bonding, (2) π-bonding, and (3) electron correlation effects. The first row (N,O) and non-first row (P,S,As,Se) elements being considered here exhibit marked differences in these categories. First, because of the high charge density and large electronegativity exhibited by the first-row elements (12), the bonds which they form with metal ions are considerably more ionic in character than are those formed by the second- and third-row elements mentioned above. It is generally considered necessary for two atoms to be of similar electronegativities in order to form good covalent bonds (13). It is noted in passing that the concept of covalency is not well defined, and is used here in the conventional sense to describe the extent of electron delocalization (14).

Both oxygen and nitrogen can function as π-donors, but not as π-acceptors. The second- and third-row elements possess low-lying, unfilled d-orbitals, which can function as π-acceptor orbitals. Finally, the greater polarizability (4) of the second- and third-row elements (implied by the lower electronegativity) leads to a lessened importance of interelectronic repulsions, and hence decreased spin-pairing energy.

The known preference of d^8 metal complexes involving the heavy donor ligands for four- and five-coordinate structures is probably a function of all of these factors. The situation for out-of-plane π-bonding is improved for the square planar and square pyramidal geometries (15). Also, the lessened interelectronic repulsions experienced with the second- and third-row donors will make less destabilizing the

electron-pairing which is necessary in the low-spin d^8 four- and five-coordinate cases. Simple covalency in these compounds is probably also a factor in stabilizing the reduced coordination numbers. It is well-documented (16) that in the strongly covalent metal-carbonyl complexes, the stable structures are those which allow completion of the "inert gas" electronic structure of eighteen valence electrons in five- and six-coordinate complexes. In the four-coordinate case, the stable electronic structure appears to consist of sixteen valence electrons. A rationalization of this result has been proposed by Orgel (16). It appears, then, that the d^8 complexes with heavy donor ligands form four- and five-coordinate complexes in order to achieve the stable electronic valence shell configuration. The tendency toward high-spin complexes with the first-row donor atoms and low-spin complexes with non-first-row atoms is a result of the electron correlation effects described above.

The intensity of the observed "d-d" bands in the electronic absorption spectrum of complexes involving heavy donor atoms has been explained in terms of the polarizability of the donor atoms or the mixing of ligand character in the molecular orbitals (MO's) derived from the metal d levels (17). Such mixing is another way of expressing the extent of covalent bonding. The intensity of "d-d" bands increases with the amount of ligand character of the two levels involved in the electronic transition. The largest contribution to the intensity of "d-d" bands comes from a one-center term involving ligand orbitals only, rather than from the so-called "charge-transfer," two-center term involving ligand and metal orbitals (18). The strong involvement of

heavy-donor orbitals is due in part to the increase in energy of the ligand σ-donor orbitals in proceeding down in the periodic table.

The apparently anomalous spectrochemical series ordering, P > N > As, has been explained (10) in terms of the π-acceptor ability of the phosphine ligand. The stabilization of the dπ level in the phosphine complex is apparently greater than the corresponding stabilization of dσ* in passing from N to P, leading to the spectrochemical series ordering, P > N.

The trans-labilizing effect observed in complexes of the phosphines is understood to be due to the effects of covalent bonding (7). Studies of the kinetic trans-effect have led to considerable speculation about σ- and π-bonding contributions to this effect, and about the extent of π-bonding in phosphine and arsine complexes in general. One additional type of evidence often cited for π-bonding in metal-phosphine and arsine complexes is the reduction of the metal-phosphorus or arsenic bond distances in complexes below the sum of the covalent radii (19-21).

More recently, the π-acceptor interpretation of phosphines and arsines has been challenged by Venanzi on the basis of his nuclear magnetic resonance (nmr) studies (22) on various complexes of tertiary phosphines with platinum(II) ($PtX_2(PR_3)_2$, $PtX_4(PR_3)_2$; R=OCH_3, n-C_4H_9). From values of the Pt-P coupling constants, he calculates the s-character in metal-ligand bonds of the cis- and trans-isomers of both the four- and six-coordinate complexes, and concludes that the observed bonding characteristics of these complexes can be adequately explained without involving π-bonding. The problems of using nmr data to interpret the kinetic trans-effect have been discussed by Langford and Gray

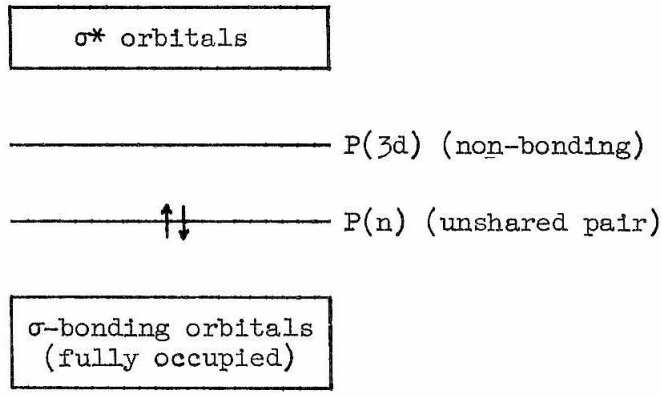
(7), and it appears that other explanations of Venanzi's data may be possible. There is general agreement, however, that the ligand PF_3 is a good π-acceptor. Complexes involving PF_3 show properties strikingly similar to the corresponding carbonyl complexes (23). The presence of the strongly electronegative fluorine atoms must contribute strongly to the electron acceptor ability of this molecule.

The true picture of the bonding in these complexes will, of course, only be known when a complete description of their electronic structure can be given. A vitally important step in determining the electronic structure of a metal complex in which covalent bonding is of importance is the determination of the electronic structure of the ligand. If the full electronic structure of phosphine or arsine molecules were known, the σ- and π-characteristics would follow at once. The traditional way in which electronic structures of ligands have been determined has been by carrying out molecular orbital calculations of various degrees of sophistication and interpreting the results in conjunction with electronic band spectra and, more recently, photoelectron ionization studies (24). The molecular orbital scheme thus derived for the ligand has then been used, in conjunction with magnetic and electronic spectral experimental results, in a semi-empirical molecular orbital (MO) calculation for the metal complex. At least one MO calculation has been carried out on a substituted phosphine molecule (25).

More recently, an alternative procedure has been developed, as a result of the growing realization that for complicated molecular systems the semi-empirical calculations are of rather limited usefulness. This method is more experimentally based and has been applied in the

case of the square-planar halides and cyanides of the nickel triad (26), the pentacyanothiocyanato complexes of cobalt(III) and iron(III) (27), and a five-coordinate nickel-phosphine complex (28). Rather than attempt any calculation on the complicated phosphine and arsine systems being examined here, we shall limit this study to a consideration of the electronic structure based on experimental results and straightforward, qualitative energy arguments.

On the basis of the known atomic orbital energies for phosphorus, arsenic, and carbon, and a purely qualitative MO picture, it is probable that for a tertiary aliphatic phosphine or arsine, the electronic structure may be crudely described in this way



Because of the large energy separation between the highest occupied and lowest unoccupied orbitals in aliphatic phosphines and arsines, electronic spectra are of no help in estimating orbital separations. In the case of aryl derivatives of phosphines and arsines, electronic spectra are useful. A comparison of the spectrum of benzene with those of triphenylphosphine and triphenylarsine points up some important differences which are dependent upon the nature of the heteroatom (Table I).

Table I

Electronic Spectra of Aromatic Arsines and Phosphines[a]

C_6H_6[b]	$(C_6H_5)_3P$[c]	$(C_6H_5)_3PO$[c]	$(C_6H_5)_3As$[c]
49,140 (7400)		44,545 (21,400)	
41,150 (84)		39,215 (Sh 1050)	
40,160 (156)	38,315 (11,000)	38,460 (1520)	40,325 (12,300)
39,295 (204)		37,665 (1960)	
38,315 (144)		36,695 (1620)	

[a] $\bar{\nu}$ cm.$^{-1}$ (ϵ, ℓ.mole^{-1}cm.$^{-1}$).

[b] From Ref. 29.

[c] From Ref. 30.

The electronic spectra of aryl-substituted compounds of the Group V elements have been studied in the past by a number of workers (30,31). Spectral data for the triaryl derivatives of the Group V elements are collected in Table I. The crude MO scheme which might be constructed for the aryl phosphine differs from the alkyl phosphine picture already presented only in that there is now in addition a set of π-bonding MO's from the aromatic rings and a set of π-antibonding MO's. A point which has been open to considerable discussion is whether or not the non-bonding electron pair on the heteroatom is at all "conjugated" with the aromatic ring π-orbitals. Cullen and Hochstrasser appear to have provided an answer to that question in some cases by a very elegant spectral study (32) which will be discussed later.

The most striking difference between the spectrum of triphenylphosphine and that of triphenylphosphine oxide is that the latter is so similar to that of benzene, while the former is quite different. The broad band in the spectrum of triphenyl-Group V derivatives has been logically attributed to the presence of the unshared pair of electrons localized on the heteroatom (30). The electronic spectra of the pentavalent phosphorus and arsenic compounds are expected to be determined completely by the aromatic substituents, as all the P or As electrons are in this case accommodated in very stable, σ-bonding orbitals. Early work on the trivalent derivatives was interpreted in terms of a model involving strong mixing between the lone pair electrons of the heteroatom and the aromatic system (30). This interpretation was based on the fact that no $\pi \rightarrow \pi^*$ transitions of the type seen in the spectrum of benzene were observed in the triaryl-Group V derivatives.

However, by substituting aryl groups by trifluoromethyl groups, Cullen and Hochstrasser obtained spectra in which two separate absorptions were observed (32). The system at lower energy was identified with the $\pi \rightarrow \pi^*$ transition of the aromatic ring, and the broad band at higher energy was assigned as an $n \rightarrow \pi^*$ "charge-transfer" type absorption. The assignment of the second band was based on two types of observed behavior. First, as the methyl groups in $C_6H_5As(CH_3)_2$ are substituted by trifluoromethyl groups, the band is blue-shifted (moves to higher energy). This is readily understood in terms of stabilization of the arsenic lone pair by the electron-withdrawing trifluoro groups. Secondly, the position of the band is solvent-dependent. The more polar the solvent, the more strongly is the band blue-shifted. This is standard behavior for a transition in which the ground state is considerably more polar than the excited state (33). Practically no difference in the $\pi \rightarrow \pi^*$ absorption was observed with different substituents and solvents. The conclusion reached in this study was that the π-system and the unshared pair in these arsines are essentially non-interacting. The same conclusion was inferred for the phosphines and stibines on the basis of spectra which had been previously reported. The only fully conjugated compound in this series was reported to be the aromatic amine, whose spectrum is rather different from the corresponding phosphine, arsine, and stibine (32). On this basis, then, one should not expect great differences in π-bonding between complexes of aliphatic and aromatic phosphines or arsines. It is worth noting that electronic spectral studies have revealed nothing concerning the role of arsenic or phosphorus d-orbitals in the electronic structure of these compounds.

As was mentioned earlier, the $\pi \rightarrow \pi^*$ transition occurs as the lowest energy absorption in the electronic spectra of these compounds. In view of a comparison of measured ionization potentials for $(C_6H_5)_3Q$(Q=As,P), toluene, and other relevant comparison compounds (see Table II), it appears that the ordering of the conventional, one-electron energy levels (ϵ_{SCF}) probably does not follow that of the spectral bands. This could be accounted for by large differences in inter-electronic repulsions in the two excited states. Data bearing on this point will be presented later. It is worth noting that Pearson and co-workers have reported discrepancies between the observed ordering of electronic spectral bands and ionization potentials for a series of tris(β-diketonate) metal(III) complexes (37). Briefly, their ionization potential measurements show that the first ionization of the metal complexes originates from a ligand orbital, while the lowest energy electronic absorption band is clearly a d-d band.

Table II

Ionization Potentials

Compound	IP	Method	Reference
toluene	8.82 eV	Photoionization	34
o-xylene	8.56	"	"
$(C_6H_5)_3P$	7.36	"	35
$(C_6H_5)_3As$	7.34	"	"
$(CH_3)_3As$	8.3	Electron impact[a]	36

[a]Values of ionization potentials determined by electron impact tend to be higher than those determined by photoionization. For example, IP = 9.23 eV for toluene, as determined by the electron impact method (34).

CHAPTER 2

ELECTRONIC SPECTRAL STUDIES OF SUBSTITUTED ARSINES

Introduction

In connection with studies on five-coordinate complexes of low spin nickel(II) with various polydentate ligands containing heavy donor atoms, we have carried out a study of certain electronic structural properties of the ligand o-phenylenebisdimethylarsine (diarsine). For the purpose of comparison, we have carried out parallel studies on two related and better-known compounds, triphenylarsine and triphenylphosphine. This work has proceeded along two lines. In Chapter 3, electron spin resonance studies of radicals produced from these compounds and other substituted arsines by uv-irradiation at low temperature are described. This chapter deals with electronic spectral studies of various types. The electronic spectrum of diarsine has been measured in solution at room temperature and 77°K, for comparison with previously reported (30) spectral results on triphenylarsine and triphenylphosphine. Also, charge-transfer complexes involving these donor molecules and the well-known π-acceptor, tetracyanoethylene, have been prepared and the spectra measured, in order to estimate relative values for the ionization potentials of the donor molecules.

Experimental

Compounds

o-phenylenebisdimethylarsine (diarsine) was prepared and puri-

fied by the method of Feltham (38a)(b.p. 102°-106°C.; 1 mm.), or obtained from City Chemical Company or Aldrich Chemical Company and used without further purification. The purity of the sample was checked by nmr and uv spectroscopy. The sample obtained from City Chemical Company was found to be decomposed after standing for several months. If refrigerated and protected from oxygen, diarsine will not significantly decompose for many months. Triphenylarsine and triphenylphosphine were both reagent grade chemicals, obtained from Aldrich and Matheson, Coleman, and Bell. Tetracyanoethylene was an Eastman Organic Chemicals white label reagent. All these samples were used without further purification.

Charge-Transfer Complexes

The charge-transfer complexes of triphenylarsine or triphenylphosphine with tetracyanoethylene (TCNE) appear to be quite stable in solution, and were prepared by simply dissolving the two components together in chloroform. Varying the proportion of TCNE to donor does not seem to affect the band positions, or the ratio of absorbance of the two bands exhibited by the charge-transfer complex. The charge-transfer complex of TCNE with diarsine is considerably less stable than the other two studied, but can be prepared and studied in the same way. The stability of the (diarsine·TCNE) charge-transfer complex is strongly solvent dependent. In chloroform, the blue color of the freshly prepared complex persists for over five minutes. In ethanol, the solution becomes yellow immediately, due to the formation of the stable radical anion $(TCNE)^{-}$. Carrying out the charge-transfer complex forming reaction in the absence of oxygen and light did not lead to noticeably

increased stability. At liquid nitrogen temperature, the equilibrium (1) is shifted far to the right,

$$\text{diars} + \text{TCNE} \overset{K}{\rightleftharpoons} (\text{diars}\cdot\text{TCNE}) \qquad (1)$$

and the complex appears to be stable for many hours.

Spectral Measurements

The ultraviolet absorption spectral measurements were made on a Cary 14RI spectrophotometer, using 1.00 cm. square cells of fused Suprasil. Measurement of spectra at 77°K. were carried out with a quartz Dewar which allowed complete immersion of the sample during the spectral measurement. Bubbling of the liquid nitrogen under operating conditions was prevented by cooling to 75°K. under reduced pressure.

Freshly prepared EPA (5 parts ethyl ether:5 parts isopentane: 2 parts ethanol) was used as solvent for the low temperature measurements. The ethanol was anhydrous U.S.P.-N.F. grade (U.S. Industrial Chemical Co.), the ethyl ether anhydrous reagent grade (Mallinckrodt), and the 2-methylbutane spectroquality (Matheson, Coleman and Bell). Chloroform used in the spectral studies of the charge-transfer complexes was spectroquality (MCB).

Results

Spectral Measurements

The electronic spectrum of diarsine shows a modest improvement in resolution in the low temperature spectrum, but no drastic changes occur. The results of the spectral study are set out in Table III. The weak shoulders which appear on the low energy side of the main absorption

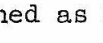
Table III

Electronic Absorption Spectrum of Diarsine[a]

T = 300°K		T = 77°K		
35,000-40,000	(400-4000)[b]	(WS)	35,160	(1280)
		(WS)	36,385	(2620)
		(WS)	37,398	(3630)
		(WS)	38,490	(4460)
			41,036	(9150)

[a] $\bar{\nu}$ cm.$^{-1}$ (ϵ,ℓ.mole^{-1}cm.$^{-1}$). EPA solvent (5:5:2 mixture of ethyl ether, isopentane, and ethanol).

[b] Featureless, rising absorption.

in each spectrum are assigned as the $\pi \rightarrow \pi^*$ transition localized on the benzene ring. The main absorption appears as a band maximum for triphenylarsine and triphenylphosphine, and as a shoulder in the spectrum of diarsine. It is assigned as P or As(σ) $\rightarrow$  (π^*) transition. These assignments for $(C_6H_5)_3Q$(Q=As,P) have been given previously by Cullen and Hochstrasser (32). The spectrum of diarsine is similar to that of $(C_6H_5)_3Q$, and is assigned in the same way.

Charge-Transfer Complexes

The spectra of the charge-transfer complexes of $(C_6H_5)_3Q$ with TCNE are pictured in Figure 1. Comparing these spectra with the data in Table III for the spectrum of the donor molecules alone and Table IV for the spectrum of TCNE and $(TCNE)^-$ alone reveals that the electronic spectrum of each of these charge-transfer complexes contains two bands. The complete results of the study of the visible spectra of the charge-transfer complexes are given in Table V.

The problem of the instability of the (diarsine·TCNE) complex has already been described. By working rapidly and carrying out the measurement of the spectrum in sections, a reasonably reproducible spectrum was obtained. It was also attempted to prepare the charge-transfer complex of diarsine with tetrachloro-p-benzoquinone (chloranil). A charge-transfer complex is formed in this case. In fact, it appears that more than one species may be formed, depending on the concentration ratio of diarsine to chloranil. At high concentrations of chloranil, a blue complex appears, and at lower concentrations, a red form is present. These could be maintained at low temperature, but were not further studied, due to rather severe problems involved in finding a suitable

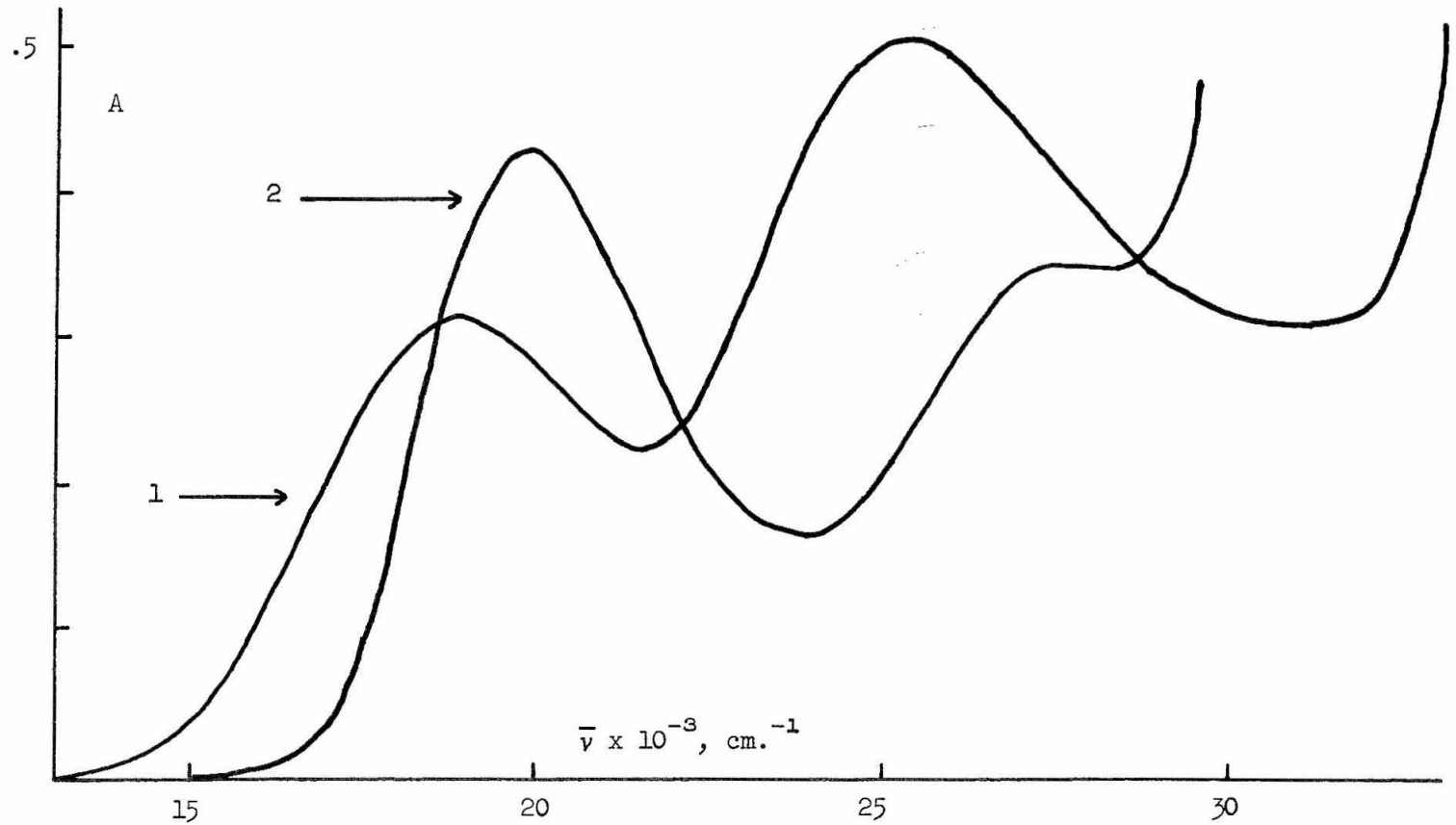


Figure 1. Electronic Spectra of Charge-Transfer Complexes in $CHCl_3$·1-[$(C_6H_5)_3As$·TCNE]; 2-[$(C_6H_5)_3P$·TCNE].

Table IV

Electronic Absorption Spectra of TCNE[a] and $(TCNE)^-$

Species	$\bar{\nu}_{max}$	ϵ
$(TCNE)^-$ [b]	21,370 $cm.^{-1}$	4400
	21,880	5670
	22,470	6520
	22,990	7100
	23,530	7100
	24,040	6890
	24,570	6200
	25,125	5460
	25,640	4660
	26,180	3810
	26,740	3070
	27,320	2440
TCNE	> 35,000 $cm.^{-1}$	

[a] TCNE = tetracyanoethylene.

[b] Acetonitrile solution; from Ref. 38b.

Table V

Electronic Absorption Spectra of Molecular Complexes[a]

Donor	Acceptor	λ_{max}	$\bar{\nu}$	A
$(C_6H_5)_3N$	TCNE	866 nm	11,545 $cm.^{-1}$	.86
		415	24,095	.86
$(C_6H_5)_3P$	"	502	19,915	.43
		374	26,750	Sh .33
$(C_6H_5)_3As$	"	530	18,885	.47
		394	25,345	.76
$[(C_6H_5)_2AsCH_2]_2$	"	532	18,795	.55
		402	24,875	1.31
diarsine	"	580	17,225	.80
		428	23,390	Sh .32

[a]Measured in $CHCl_3$ solution, 300°K.

solvent for measuring the spectrum at 77°K. It seems likely that a suitable solvent mixture could be found upon further investigation. It would be worthwhile to determine the nature of the complexes formed here. At room temperature, the initial color is gone in seconds. As with the diarsine-TCNE system, involved chemical reactions seem to accompany the breakup of the charge-transfer complex, as is evidenced by the striking color changes, solids formed, etc. The diarsine-chloranil system in chloroform changes color and deposits colorless crystals within a few minutes. After a matter of hours a black solid separates from the deep purple solution which is formed. No speculation will be offered concerning the nature of these reactions, but it appears that the system could be the subject of rather extensive mechanistic studies. Detailed work has been carried out on the reactions of a similar system, chloranil and dimethylaniline (39).

Diarsine does not form a charge-transfer complex with p-benzoquinone. It was also attempted to prepare a complex of TCNE with trimethylphosphine. However, charge-transfer appears to occur at once, giving $(TCNE)^-$ and other, unknown products.

Discussion

Benesi and Hildebrand first presented physical evidence for the relatively weak intermolecular interactions which lead to the formation of the so-called molecular complexes, or charge-transfer complexes (40). They reported an absorption band in the spectrum of a solution of iodine in benzene which was characteristic of neither component. Since that time, a large number of complexes between electron donor (D) and electron acceptor (A) molecules have been reported. A method for

determining the formation constant K_C and ϵ for the complex has been reported (40), and a quantum mechanical

$$D + A \overset{K_C}{\rightleftharpoons} (D \cdot A) \qquad (2)$$

description of the ground state and charge-transfer excited state given (41). Two monographs and a review article have appeared which give a general review of the field (39,42-43). While a number of techniques have been applied to the study of the molecular complexes, the principal method for obtaining information about the electronic structure remains electronic absorption spectroscopy.

In 1953, McConnell and coworkers pointed out the relation between the energy of the charge-transfer transition in the spectrum of the complex and the ionization potential of the donor molecule (44). They found that if the ionization potentials lie within a relatively small range ($\pm$ 1-2 eV), this relation may be expressed as

$$h\nu_{CT} = I_D + b \ . \qquad (3)$$

The relationship has been seen to be obeyed by complexes involving trinitrofluorenone, tetracyanoethylene, and iodine as acceptor, for a series of substituted benzene donor molecules (43).

The work reported here on the molecular complexes of these arsines and phosphine with TCNE could be extended to include a complete concentration-dependence study of the type carried out by Augdahl and coworkers on the charge transfer complex of iodine with triphenylarsine (45). This type of study would yield the values of K_C (eqn. 2) and ϵ for the complexes (46). An important experimental result which can be obtained without such a study, however, is the relative ionization

potentials of the donor molecules, as determined by the position of the charge-transfer band. Examination of the data in Table V clearly indicates that the band position energy ordering is $(C_6H_5)_3P > (C_6H_5)_3As >$ diarsine, with differences of least 1000 $cm.^{-1}$ in each case. Because the same acceptor is used for all the charge-transfer complexes, the band position energy ordering should vary in the same way as the ionization potential of the donor, so that in terms of ionization potential, the ordering should then be $(C_6H_5)_3P > (C_6H_5)_3As >$ diarsine. This ordering is certainly in accord with a simple prediction based on the relative energies of arsenic and phosphorus lone pairs and the inductive effects of aryl and alkyl groups on electron donor properties. Voigt and Reid have correlated the position of the charge-transfer absorption with the ionization potential of the donor for a number of molecular complexes involving TCNE as acceptor (47). This study used a number of substituted benzene molecules as donors. For this set of compounds, they report values of m = 0.83 and b = 4.42 for the parameters of eqn. 3. They point out that similar compounds to those studied must be used if these values are going to be applied in eqn. 3 to estimate I_D. On the other hand, Hastings and coworkers (48) have reported a correlation between the energy of the charge-transfer transition and ionization potential of the donor which is reasonably linear for a wide variety of donors. These workers have prepared and studied molecular complexes of iodine with alkyl halides, alcohols, saturated hydrocarbons, ethers, olefins, aromatic hydrocarbons, and thioethers. It is perhaps worth calculating values of I_D for the compounds under study here, using the values of m and b determined by Voigt and Reid. This is not strictly

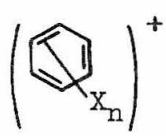
correct because the charge transfer transition in this case originates on n orbitals. Using these values in equation 3, and the energy of the lowest energy charge-transfer band from the spectra in Table III, we obtain

Compound	$\tilde{\nu}$	I_D
$(C_6H_5)_3P$	19,916 cm.$^{-1}$	8.30 eV
$(C_6H_5)_3As$	18,883	8.15
diarsine	17,226	7.90

These values are within 1 eV of the values collected in Table II, which is reasonable, considering the assumptions made. The ordering of these ionization potentials is reliable.

This ordering of ionization potentials results in the reverse ordering of the donor orbitals in the electronic structural scheme for the molecules, diarsine > $(C_6H_5)_3As$ > $(C_6H_5)_3P$. A comparison of these charge-transfer band positions with that of the (TCNE·toluene) complex ($\tilde{\nu}_{max}$ = 24,600 cm.$^{-1}$) indicates that the lowest energy band in the spectrum of the TCNE-arsine or phosphine complex must be due to charge transfer from the unshared pair on the heteroatom, rather than from "benzene" π-orbitals. On the basis of the relative energy positions of the heteroatom donor level in the phosphine and arsines, one might naively expect the position of the n → π* transition in the spectrum of the phosphine or arsine alone to appear as the lowest energy band in the spectrum, and to vary in the order diarsine > $(C_6H_5)_3As$ > $(C_6H_5)_3P$. This transition has been assigned to the intense band in these spectra, which is not the lowest energy band, and the observed energy ordering is

$(C_6H_5)_3P < (C_6H_5)_3As \sim$ diarsine. A conventional explanation of the observed trend is based on interelectronic repulsion effects. These are so large that they are seen to be the dominant factor in determining band position orderings within the spectrum of each compound, reversing the ordering predicted on the basis of the one-electron energy levels (ϵ_{SCF}). A qualitative electron repulsion argument indicates that the effect operates in the direction required to rationalize the anomalous ordering of the $n \rightarrow \pi^*$ energies in $(C_6H_5)_3As > (C_6H_5)_3P$.

It was noted that the electronic spectra of these charge-transfer complexes exhibit <u>two</u> bands which do not appear in the spectrum of either of the components. A similar effect has been reported for charge-transfer complexes involving substituted benzene donor molecules (47). This effect was first interpreted by Orgel (50) as due to a splitting in the charge-transfer excited state which should appear because of the lifting of the degeneracy of the "ground state" or  species by the presence of the substituent(s). For the complexes under consideration here, it is probably more nearly correct to consider the two charge-transfer transitions as arising from charge transfer processes originating from two types of donor orbitals. The lower energy band originates in the arsenic or phosphorus lone pair orbital and the higher energy band in the highest filled aromatic π-bonding orbital. The position of the charge transfer absorption in the TCNE-benzene complex is 25,800 $cm.^{-1}$ and in the toluene complex is 24,600 $cm.^{-1}$, in quite reasonable agreement with the band positions recorded for the second band in the TCNE-arsines and phosphine complexes (see Table V).

CHAPTER 3

ELECTRON SPIN RESONANCE STUDIES OF uv-IRRADIATED SAMPLES OF SUBSTITUTED ARSINES

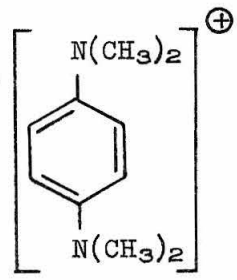
Introduction

Electron spin resonance (esr), electronic spectral, and polarographic measurements on the transition metal-dithiolene complexes have led to the conclusion that the ease of electron-transfer processes in these systems is a result of the nature of the ligand system (11,51-53). In particular, it has been suggested that certain paramagnetic metal-dithiolene complexes (formally d^7) are actually better described as composed of "oxidized radical ligands" complexed with diamagnetic (d^8) metal ions (54). Some controversy over this characterization has given rise to a considerable amount of imaginative work (11,55). The conclusion of the matter appears to be that these highly delocalized systems can only be properly described in terms of molecular orbitals and to speak of the oxidation or reduction process as being localized exclusively on the metal ion or the ligands is an oversimplification (55).

It has been known for almost twenty years now that the diarsine ligand forms a very stable, six-coordinate, nickel complex which, if described in the traditional fashion is a d^7, nickel(III) complex (56). The apparent similarity between the dithiolene ligands and diarsine has led to speculation that this complex is perhaps best described not as d^7 nickel(III), but as d^8 nickel(II) coordinated to an oxidized radical

ligand system. The ionization potential of the donor atom is lower in diarsine than in the dithiolenes, and thus it was thought that there might be a greater contribution of ligand orbitals to certain MO's derived from the metal d-orbitals in the diarsine complexes than in the dithiolenes. Detailed studies on the molecular and electronic structure of the dichlorobis-(diarsine)-nickel monocation have been carried out in these laboratories, including an X-ray structural determination (57) and single-crystal esr study (58). Because of the possibility of describing this complex as one in which the unpaired electron resides mainly in ligand orbitals, it was decided to attempt to generate and study the isolated "oxidized radical ligand," the radical cation $(diars)^+$. A comparison of the esr spectrum of this species with that of the paramagnetic nickel complex was expected to aid in describing the electronic structure of the complex. It is also possible that information about $(diars)^+$ might help to better understand the electronic structure of diarsine. It is apparent that any such extrapolations must be made with great care.

The production of radical ions from neutral molecules has been carried out using a number of techniques. The most widely applicable have been chemical redox processes (59), electrochemical methods (60), photolysis with ultraviolet or visible light (61) and x- or γ-irradiation (62). In view of the probable instability of $(diars)^+$, it was decided to use a method which allows in situ production of the radical at low temperature in a rigid matrix, namely uv photolysis. In order to explain the nature of the experiment and to anticipate certain results, the well-studied case of the radical cation of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), Würster's blue ion (WB) is described below.



(WB)

This species (WB) has been known for many years. It exhibits great stability, persisting in aqueous solution for long periods of time. It was first prepared by chemical oxidation using bromine (59), and has since been generated using a large number of standard physical techniques. Lewis and Lipkin include WB as a calibration compound in their classic paper on "photooxidation" of substituted aryl amines (61). The electronic absorption spectrum of WB is well-established, and at 90°K in EPA consists of a structured band centered near 600 nm. Its esr spectrum has also been the subject of considerable study and the interpretation has been settled, after some initial confusion. Computer simulation analysis of the spectrum has yielded for the hyperfine splitting constants, A^{N} = 6.99 G., A^{CH_3} = 6.76 G., A^{H} = 1.97 G. (63). This indicates that while the unpaired spin is delocalized throughout the molecule, most of the time it is on the $-N(CH_3)_2$ group, as would be expected from electronegativity considerations. The ease of producing the TMPD cation correlates well with known results on charge-transfer complexes involving this molecule as donor. TMPD is generally regarded as the most powerful organic donor molecule known. The low ionization potential of the molecule is reflected in the extremely low values recorded for the charge-transfer maxima when

combined with acceptors (TMPD·chloranil, λ_{C-T} = 953 nm; TMPD·TCNQ, λ_{C-T} = 1163 nm) (49). In view of the structural similarity of diarsine to TMPD, and the relatively low energy position of the charge-transfer band in (diarsine·TCNE), λ_{C-T} = 581 nm, similarities in behavior between the two compounds are expected. In particular it was hoped that the relatively low ionization potential of diarsine would allow the application of uv-photolysis to the problem of generating $(diars)^+$.

The phenomenon of photoionization may at first glance seem to be in contradiction with the known ionization potentials of molecules. This problem has been discussed by Hamill and coworkers, who point out that while the ionization potential of N,N'-dimethyl-p-phenylenediamine (DMPD) is reasonably estimated to be 7.5 eV, it is quite possible to generate the cation of this molecule by uv-irradiation with photons of energy as low as 4 eV (64). While contributions from polarization energy of the ions and the electron affinity of the acceptor are important, bond breaking in the acceptor tends to cancel these and a sizable discrepancy (1-2 eV) is still present. Apparently an important feature of the "photooxidation" is that the resulting positive and negative species are locked in a rather tight ion-pair by the rigid matrix. The stabilization derived from this ion-pairing is regarded as sufficient to make up the apparent energy deficit predicted on the basis of this crude model.

The mechanism of the photooxidation has been the subject of experiment and speculation, and is discussed by Meyer and Albrecht (65). They have studied the case of TMPD in a frozen solution using 3-methylpentane as solvent. Because the near-uv absorption spectrum of a solu-

tion of the donor (D) in a solvent (A) may be attributed to the donor alone, it is apparent that the primary process in the photoionization is excitation of the donor, $DA_n \xrightarrow{h\nu} D^*A_n$. Their studies of the variation of quantum yield with wavelength indicate the coincidence of the onset of photooxidation with the onset of absorption for both TMPD and p-phenylenediamine. They have also found when polarized light is used to carry out the photooxidation of TMPD, the polarization corresponding to that exhibited by the lowest energy absorption band in TMPD is the most effective (65). Following excitation of the donor molecule, the energy barrier between this state and the charge transfer state is tunneled or surmounted, $D^*A_n \rightarrow (D^+, A_n^-)$ to give the ion-pair which is stable in the rigid low-temperature matrix. It is apparent from studies involving electron acceptors as additives to solutions of donor molecules that this initial charge transfer process can be followed by further steps. One such process has been described by Hamill as "dissociative electron attachment" (64). This is exhibited in solutions of an aromatic amine donor molecule (DMPD) and an electron acceptor molecule (CCl_4 or $C_6H_5CH_2Cl$). The (D^+, A^-) ion pair, where A is now the added acceptor rather than the solvent, in this case rapidly falls apart to give more stable products. For example, $C_6H_5CH_2Cl^{\ominus}$ goes to $C_6H_5CH_2\cdot + Cl^{\ominus}$ immediately.

Further evidence that photoionization yields relatively fixed ion clusters is given by the observed solvent dependence of the efficiency of photoionization as compared with that of ionization caused by high-energy radiation (x-,γ-rays). Photoionization is best promoted by polar solvents, and γ-ionization occurs most readily in nonpolar solvents (62). The study of various defect or "color" centers produced in the

high-energy irradiation of materials of all types is a well-developed field (62,66). In this process, there is extensive delocalization of electrons or "holes" ejected from molecules on the incidence of high-energy radiation. The electrons are excited high into the continuum, and so can migrate freely throughout the material. The localized ion-pairs which must be present in photoionization are not formed in this case. Such a process should be favored by a nonpolar medium, in which there is not a strong field of charges which would tend to trap the migrating electrons or holes rapidly. In the case of photoionization where localized ion pairs are formed, these would obviously be more stabilized (higher polarization energy) in a polar medium.

The main problem in studies of radical species produced by radiation damage, of either the high energy or ultraviolet type, is identification of the species produced. This is usually possible by a combination of esr and electronic absorption spectroscopy, but very often ambiguities concerning the assignment of the spectra remain. Electronic structural results based on such studies must be considered less reliable than those using well-characterized compounds, because identification errors can easily be made. The way in which the identification process is ordinarily carried out is to examine the spectroscopic results obtained and try to match these with those expected for the molecular fragments and ions which could conceivably be produced from the starting material. It would be well to examine some studies of this type which have been carried out.

Experimental results have been obtained for a large number of radicals containing carbon, hydrogen, oxygen, and nitrogen (66,67) and

also for inorganic radicals produced by x-irradiation of crystalline materials (68). There has also been some work done on compounds containing the heavy donor atoms sulfur and selenium. The sulfur and selenium radicals exhibit esr spectra which are rather different from those seen for simpler organic radicals. The spectra of the organic radicals are typically sharp, highly split patterns, with very small anistropy. The signals arising from the aliphatic sulfur-containing radicals are quite broad, do not show hyperfine splitting, and exhibit a rhombic g-tensor ($g_{xx} \neq g_{yy} \neq g_{zz}$) in the powder or glass spectrum. An example of this type of behavior is the paramagnetic species produced by γ-irradiation of crystalline L-cystine hydrochloride. The product in this case is thought to be $\left(HOOC-\underset{NH_2}{CH}-CH_2S\cdot \right)$, produced by cleavage of the disulfide bridge bond. The observed spectrum exhibits a rhombic g-tensor $g_1 = 2.003$, $g_2 = 2.025$, $g_3 = 2.053$ (69). These g-values are very close to those obtained from x-irradiated single crystals of 3,3'-dithiopropionic acid. This esr spectrum exhibits $g_1 = 2.003$, $g_2 = 2.025$, $g_3 = 2.055$, and is assigned to the fragment ($HOOCCH_2CH_2S\cdot$), also produced by cleavage of the disulfide bond (70). This is the most likely radical which could give rise to a rhombic g-tensor. The known studies involving selenium radicals report an axially symmetric g-tensor. Ultraviolet irradiation of di-n-dodecylselenide yields a broad signal, $g_{11} = 2.12$, $g_1 = 2.08$, attributed to ($CH_3(CH_2)_{11}Se$) (71). No explanation for the difference in g-tensor symmetry between sulfur and selenium radicals has been given.

There have been three esr studies of paramagnetic transition metal-arsine complexes in which hyperfine splitting due to ^{75}As was reported. The case of ($Ni(diars)_2Cl^{2+}$) has already been mentioned (57).

The other examples are $[CrClNO(diars)_2]^+$, for which $\langle A_{As} \rangle$ = 37.5 G. (72), and $VCl_3[(C_4H_9)_2As\text{-}CH{=}CH_2]_n$, with $\langle A_{As} \rangle$ = 29 G. (73). X-irradiation of a single crystal of Na_2AsO_3 gives rise to a paramagnetic species identified as $\cdot AsO_3^{2-}(C_{3v})$. The esr spectrum reported exhibits very large arsenic hyperfine splitting $\langle A_{As} \rangle$ = 619 G. The other relevant parameters are $g_{\parallel}$ = 2.004, $g_{\perp}$ = 2.005, A = 725 G., B = 567 G. (74). γ-irradiation of arsine and perdeutero-arsine at 4.2°K has permitted the identification of the esr spectrum of the arsenic atom ($^4S_{3/2}$). A four-line spectrum is observed, with $\langle A \rangle$ = 11.2 g. (75). Theoretically, the S state atom is not expected to exhibit nuclear hyperfine splitting. The relatively small isotropic value observed is the result of the configuration interaction with states of nonzero orbital angular momentum. γ-irradiation of the corresponding phosphines yields the fragments PH_2 and PD_2, as well as phosphorus and hydrogen atoms. The observed hyperfine splitting observed for PH_2, $\langle A_P \rangle$ = 80 g., $\langle A_H \rangle$ = 18 g., leads to the conclusion that the MO which contains the unpaired electron has < 2.2°% phosphorus s-orbital character, and the bonding orbitals have 27% s-character. A calculation of the bond angle based on the s-electron spin-polarization for the proton hyperfine splitting yields a value of θ = 112° (75). This is considerably higher than the value of θ = 92°27' measured for PH_3 (76). The authors conclude that this discrepancy is probably due to small d-orbital contributions in the bonding of PH_2 and PH_3, which are not taken into account in the calculation of bond angle from s-orbital character, and which could have an important effect on the bond angle.

Experimental

Reagents

Dimethyliodoarsine was prepared by the method of Burrows and Turner (77), and used without further purification. Bis(diphenylarsino) ethane was obtained from Strem Chemicals. All other reagents are the same as those which have been previously described.

Sample Preparation

Solutions have been mixed under nitrogen atmosphere and in air. The experimental results indicate no need for making up these samples under nitrogen. All solutions were thoroughly outgassed on an oil diffusion-pumped vacuum system, using the conventional freeze-pump-thaw procedure and sealing off the sample while pumping, during the third freeze cycle. The diffusion pump (Edwards Speedivac) normally attains a pressure of $\sim 10^{-6}$ mm. at the intake manifold (measured with a Penning cold cathode discharge gauge). Pressures in the sealed tubes (at 77°K) are estimated to be $\leq 10^{-5}$ mm. Each sample was sealed in a round, quartz esr tube (3 mm. I.D.), obtained from Varian Associates, Inc., to which was attached an $\overline{\$}$ joint, by means of a quartz to pyrex graded seal. These tubes were prepared by the Glass Instrument Laboratory of the Division of Chemistry and Chemical Engineering at Caltech. These quartz tubes, and the quartz Dewar described below, have been checked and show no esr signal, with or without uv-irradiation.

Irradiation of Samples

All samples were irradiated with a high pressure mercury-xenon source (Hanovia, 2.5 KW., compact arc) filtered through a 0.1 M. aqueous

cobalt(II) chloride solution to remove visible and infrared radiation. The light used in the irradiations consists of a broad band in the region 210-450 nm, with maximum intensity in the range 300-400 nm. The filtered light beam was collimated by a series of quartz lenses and focused on the sample, which was located in the center of the front compartment of the esr cavity. A hole in the front of the cavity covered with a quartz faceplate allowed access of the light beam. Using this apparatus, irradiation may be carried out during the course of the esr experiment, or alternatively the beam may be blocked while the spectrum is recorded.

Esr Measurements

Esr measurements at X-band (~10 Gc) were carried out on a Varian V-4502 spectrometer system employing 100 Kc field modulation and a 9-inch Varian electromagnet with Fieldial. This system was equipped with a V-4532 Dual Sample Cavity. Microwave frequencies were measured directly using a wave meter attached to one arm of the "Magic Tee" detection system. The magnetic field was calibrated by the measurement of a standard sample of diphenyldipicrylhydrazyl (K and K Chemical Co.) in benzene placed in the rear compartment of the dual cavity assembly. This measurement was carried out simultaneously with every spectrum measured, by using low frequency (20-400 cps) modulation and detection. This instrument, and the uv-irradiation apparatus described above, are in the laboratories of Prof. George S. Hammond of Caltech. Temperature control was achieved using the Varian V-4540 variable temperature controller. Cooling of the sample was effected by blowing a stream of pure nitrogen gas, which was first passed through a liquid nitrogen heat exchanger, through

a small quartz Dewar, which sits in the esr cavity and holds the sample tube. Calibration of the temperature controller was carried out using a standard copper-constantan thermocouple and a Leeds and Northrup millivolt potentiometer. The lowest temperature accessible under operating conditions was found to be 96°K.

Results

o-phenylenebisdimethylarsine (diarsine)

The esr spectrum of a 0.1 M. frozen solution of diarsine in ethanol (T = 96°K) after uv-photolysis for 2:00 minutes (210 nm < λ < 450 nm) is shown in Figure 2. Expanding the scale and examining the signal centered at g = 2.075 reveals seven overlapping hyperfine lines, $\langle A \rangle$ = 11.5 G., superimposed on the signal. This is pictured in Figure 3. This experiment has also been done using methylcyclohexane, MP (3:2 isopentane/methylcyclohexane), and 6:5 ethanol/methanol as solvent, and with diarsine neat. The solvent dependence of the observed spectrum has provided a useful way to distinguish between signals arising from different species. The highly split pattern of narrow lines centered at g = 2.00 is found to be strongly dependent on solvent, while the appearance of the rest of the spectrum is not. It is concluded that the radicals which give the highly split pattern must be produced from the solvent. The isotropic appearance of these signals, the narrow linewidth, and the proton hyperfine splitting observed is quite consistent with this interpretation. The band shapes are typical for radicals containing only carbon, hydrogen, and oxygen. The remaining signals are rather broad and exhibit g-values quite different from 2.00. This is as expected for

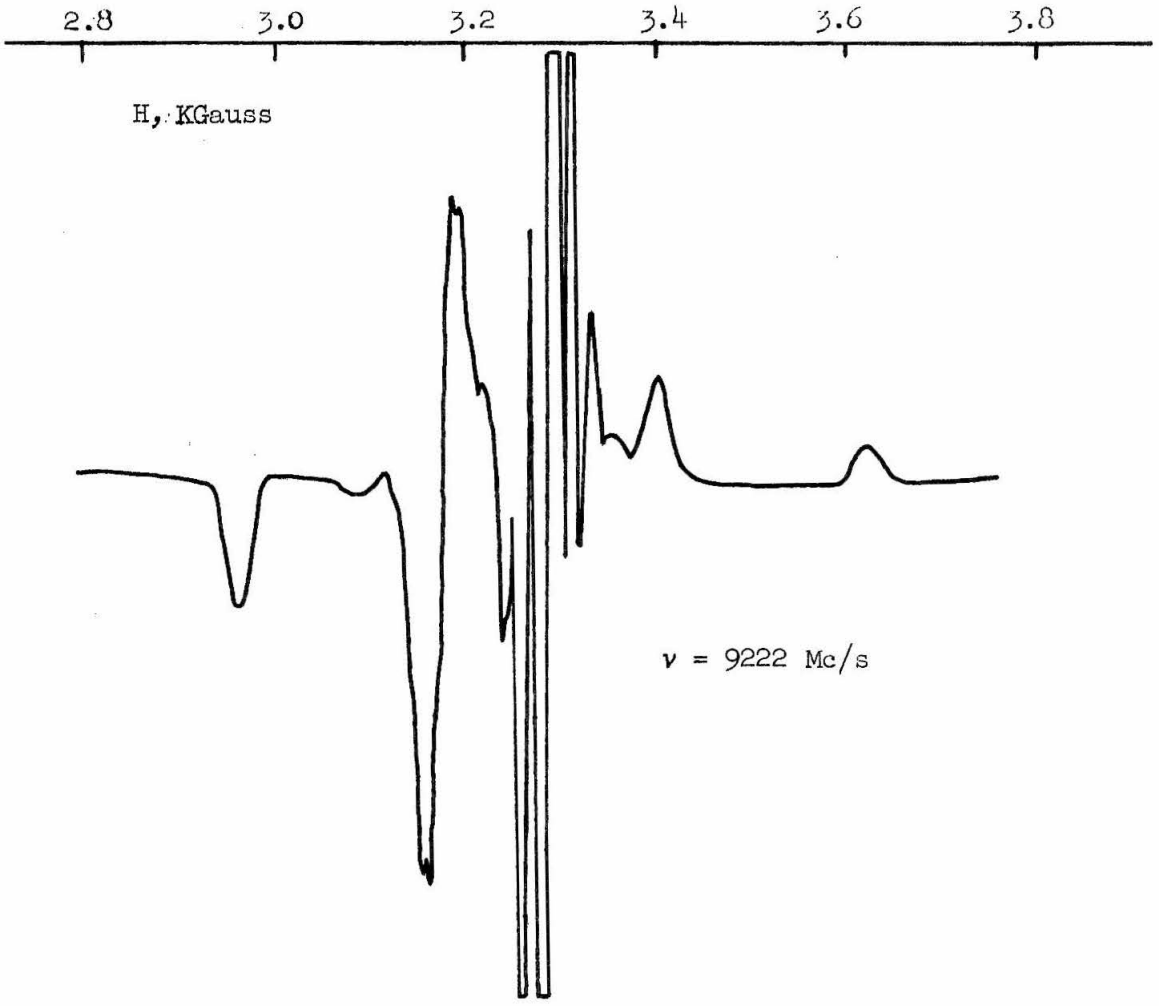


Figure 2. Esr spectrum of uv-irradiated diarsine in ethanol (96°K).

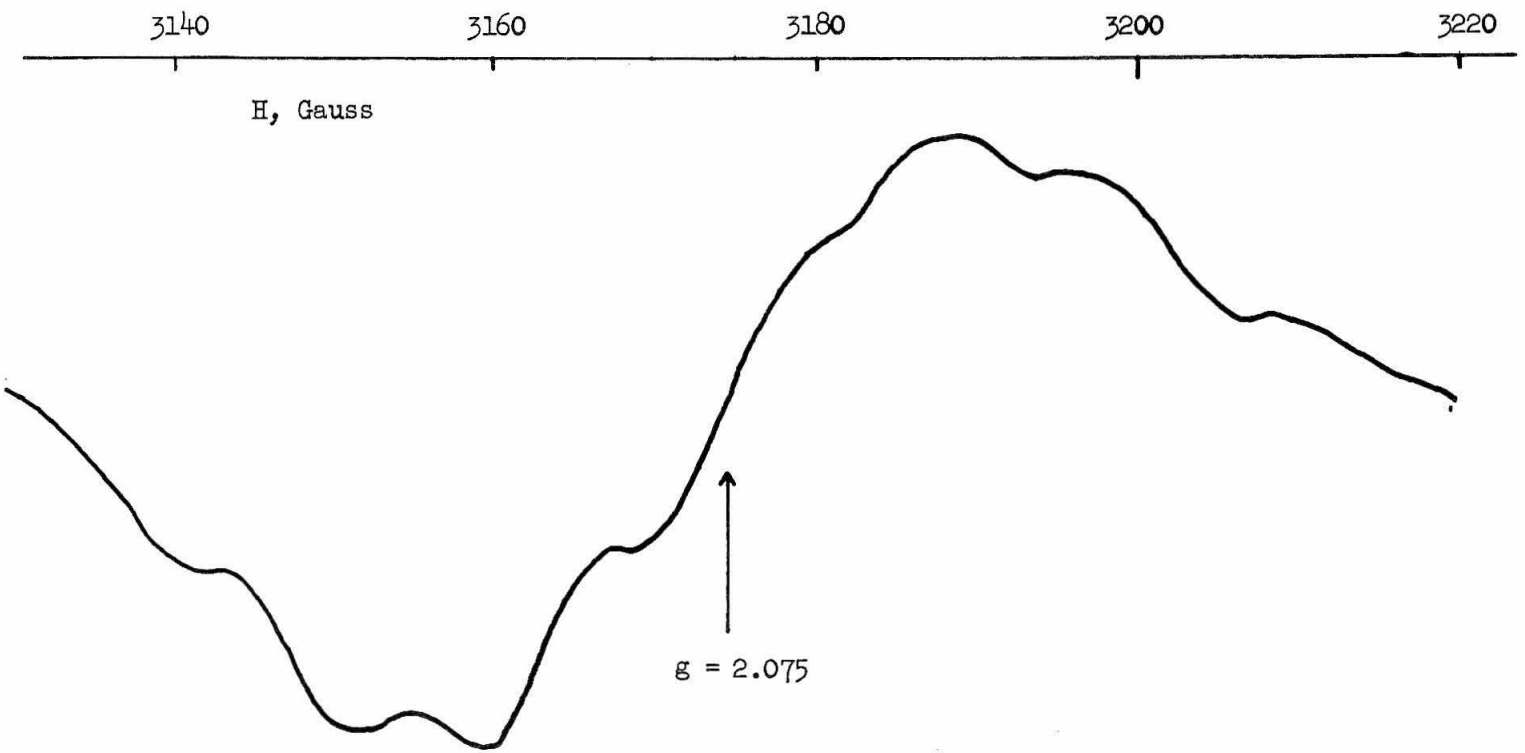


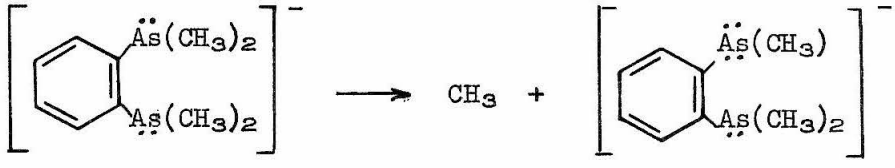
Figure 3. Esr Spectrum of $(diars)^{+}$ (expanded scale).

radicals containing arsenic, with its quadrupole moment and anisotropic charge distribution.

The presence of more than one kind of radical is consistent with expectation. Recalling the mechanism proposed for the photooxidation process, $(A,D) \rightarrow (A^-,D^+)$, we note that it is required that two radical species be formed by this process. The initially formed $(A)^-$ may rapidly proceed to $(B\cdot) + (C)^-$ in the process known as "dissociative electron attachment." This process apparently occurs here, for the proton hyperfine splitting pattern observed $\sim g = 2.00$ is never consistent with that expected for $(Solvent)^-$. The question of whether the solvent really acts as donor or acceptor will be discussed in some detail later. A particularly revealing experiment is the uv-irradiation of diarsine neat at 96°K. Diarsine is a liquid and forms a relatively clear glass at liquid nitrogen temperature. The portion of the esr spectrum near $g = 2.00$, in which solvent radicals generally appear, exhibits the four-line spectrum characteristic of methyl radical. Smaller and Matheson report $a_H = 27$ G. for CH_3 in solid methane (20°K) and $a_H = 25$ G. for uv-irradiated $(CH_3)_2Hg$ (77°K) (78). We measure $a_H = 25.1$ G. in this case (96°K). There is only one possible source of methyl radical in this one-component system. One might have expected this experiment to give $(diars)^+$ and $(diars)^-$ alone. That it does not leads to the following conclusion: either $(diars)^+$ or $(diars)^-$ is unstable under these conditions and falls apart at once to give methyl radical plus a diamagnetic ion. The possibility of production of methyl radical by bond scission is ruled out because methyl radical is not observed when diarsine is irradiated in ethanol or in the methanol-ethanol mixture. The stability of divalent arsine anions of

the form $(R_2As)^-$ is well known (79). These species are isolable as alkali metal salts and are very important reaction intermediates in preparative arsine chemistry, including the preparation of diarsine itself (38). This fact leads us to predict that the stable diamagnetic ion produced is an anion. A possible mechanism for the process is the following:

$$2\ \text{diars} \xrightarrow{h\nu} (\text{diars})^+ + (\text{diars})^-$$



If the radical anion is unstable, as depicted in this mechanism, the stable radical yielding the seven-line signal must be $(\text{diars})^+$. The similarity of the esr of the arsine radical region in all the solvents used indicates that $(\text{diars})^+$ must be present in all the cases. If this is so, diarsine acts as the donor molecule and the solvent as the acceptor in these cases also.

In ethanol, the solvent radical exhibits a regular five-line pattern (a_H = 24.5 G.), with each line showing incipient further splitting to a doublet. A quintet has been observed in the esr spectrum of γ-irradiated ethanol (a_H = 22.3 G.), and assigned to the radical $CH_3\dot{C}HOH$ (78). We assign the quintet observed here in the same way. In some cases, the ethanol solution seems to exhibit a triplet instead of a quintet. Closer examination reveals the outer lines of the quintet, with a_H = 23.5 G. Further evidence for these assignments is provided by

our observation that each of the quintet lines shows incipient further splitting to a doublet ($a_{H'}$ = 4-6 G.), which is presumably due to the hydroxyl proton.

In methylcyclohexane, the solvent radical region is extremely complicated, and it appears that more than one radical is produced. In the mixed solvent MP (3 parts isopentane/2 parts methylcyclohexane), however, it is clear that one species, methyl radical, dominates. That this is the case illustrates an interesting point concerning the photo-induced electron transfer process, namely that all possible electron transfer processes need not occur, only the most favorable. It is apparently more favorable to transfer the electron to isopentane and to produce methyl radical plus the anion from isopentane than to transfer the electron to methylcyclohexane and proceed from there. Otherwise, one would expect to observe radicals from both compounds, in proportion to the composition of the solvent mixture. Production of methyl radical is in all likelihood accompanied by production of the secondary carbanion $(CH_3\ddot{C}HCH_2CH_3)^-$.

Except for the region near g = 2.00, the esr spectrum of diarsine irradiated at 96°K is solvent-independent. The spectrum in ethanol is displayed in Fig. 2, and the positions, line shapes, and relative peak heights are listed in Table VI. The spectrum is rather complicated, and it seems unlikely that all the signals present arise from one species. An unusual feature of the spectrum is the shape of a number of the lines, which are not full derivative curves, but appear as only minima or maxima. This lineshape is characteristic of the overlapped spectrum produced by identical radicals in different orientation, which resonate

Table VI

Esr Data on uv-Irradiated Arsines

$(C_6H_5)_3As$	$[(C_6H_5)_2AsCH_2]_2$	Diarsine	$(CH_3)_2AsI$
(A) Signals Assigned to Molecular Radical Cation (g-values)			
2.079	2.078	2.075	2.076
2.074	2.072	2.041	
2.063	2.063		
(B) Other Signals Observed			
2.222	2.223	2.228	2.218
2.104 weak	2.104 weak	2.127 weak	(2.152)
2.038	2.039	2.041	
1.933	1.937	1.934	1.942
1.816	1.818	1.814	1.812

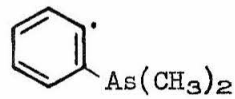
at different values of the magnetic field (H). Such an effect occurs when the g-tensor is anistropic, and is commonly observed for paramagnetic transition metal complexes (80). An alternative explanation is that these lines correspond to the outermost components of the hyperfine splitting of a signal split by the ^{75}As (I=3/2) nuclear spin. If the linewidths and splittings are of the correct size, a lineshape such as this might be obtained. This explanation is perhaps more attractive since it does not require the assignment of distinct g-values as far removed from the free-electron value as 2.22 and 1.83 to arsenic radicals. It is unfortunate that the species which give rise to this esr spectrum are unstable in liquid solution, because observation of the isotropic solution spectrum would distinguish between these alternatives.

The seven-line splitting of the most intense signal indicates the presence of two arsenic atoms (I=3/2+3/2; 2I+I=7) in the radical corresponding to this signal. Evidence has been presented in favor of assigning this species as $(diars)^+$. There is additional supporting evidence which indicates that $(diars)^+$ should be formed. The main point of this evidence is that arsines are strong electron donors, and that the initial charge-transfer process should be the transfer of an electron from the arsine to some acceptor. First, the ionization potentials of $(CH_3)_3As$ and $(C_6H_5)_3As$ are 8.3 and 7.3 eV respectively (31), while those for 1-propanol, n-octane, 2,3-dimethylbutane, cyclohexane, and ethyl ether all lie between 10 and 11 eV (62). Also, arsines function as donors in charge-transfer complexes such as those described in Chapter 2. Finally, photoionization experiments described below show that the electron-transfer takes place much more readily for diarsine and triphenyl-

arsine than for triphenylphosphine. This is in agreement with expectation if the arsine and phosphine function as electron donors, because the ionization potentials of diarsine and triphenylarsine are lower than that of triphenylphosphine. This ionization potential ordering is based on the study of molecular complexes reported in Chapter 2. One might suppose that the arsine could function as an electron acceptor as well as a donor. However, mixing of triphenylarsine with the powerful donor TMPD produces no charge-transfer complex, indicating that the arsine is not a good acceptor. Thus in all likelihood the strong signal with the seven hyperfine lines is due to $(diars)^+$ and not $(diars)^-$.

Because of the complexity of the observed esr spectrum, attempts were made to separate signals suspected of arising from different species. The solvent dependence of the region $\sim g = 2.00$ showed that the radicals in this region came from the solvent. Attempts to separate any of the other signals in the spectrum from one another did not meet with success. Under all the varying conditions tested, the relative intensities of the important signals (as measured by peak height) were not changed. The length of irradiation time was varied from 10 seconds to 1 hour, the light beam was filtered through different solutions to vary the wavelength of the incident radiation, the sample was warmed to partially destroy the radical species, and the spectrum always changed uniformly. It was not possible to destroy one signal and maintain others. The various signals all behaved as if they corresponded to the same species. Because the spectrum is independent of irradiation time, it seems unlikely that there is present both a radical decomposition product of $(diars)^+$, and $(diars)^+$ itself. If this were the case, one would

expect the proportion of the decomposition product to increase with irradiation time. Another process which may occur is bond scission. The arsenic-carbon bond is not very strong (D=51-61 kcal./mole) (31), and scission of the more stable carbon-nitrogen bond in some aromatic amines has been proposed to account for some observed photolytic results (81). Cleavage of one of the phenyl-arsenic bonds in diarsine would give rise to two radicals, each containing one arsenic atom, either of which might react further with the solvent,



(I)

$(CH_3)_2\ddot{A}s\cdot$

(II)

A way of testing to see whether this process occurs might be to try to produce (II) alone by photolyzing $[(CH_3)_2As]_2$ in frozen solution and observing the esr spectrum. For the As-As bond, D = 38 kcal./mole (31). Results obtained with other substituted arsines are important in the assignment of the esr spectrum of uv-irradiated diarsine, and are discussed below.

Triphenylarsine

The esr spectrum of a uv-irradiated sample of triphenylarsine in ethanol is shown in Figure 4. The gross features of the spectrum are remarkably similar to those observed for diarsine. The positions of all the corresponding maxima and minima, and of the main arsenic radical signal are all nearly identical in the two cases. The appearance of the main signal ($g \approx 2.07$), however, is different. There is no seven-line

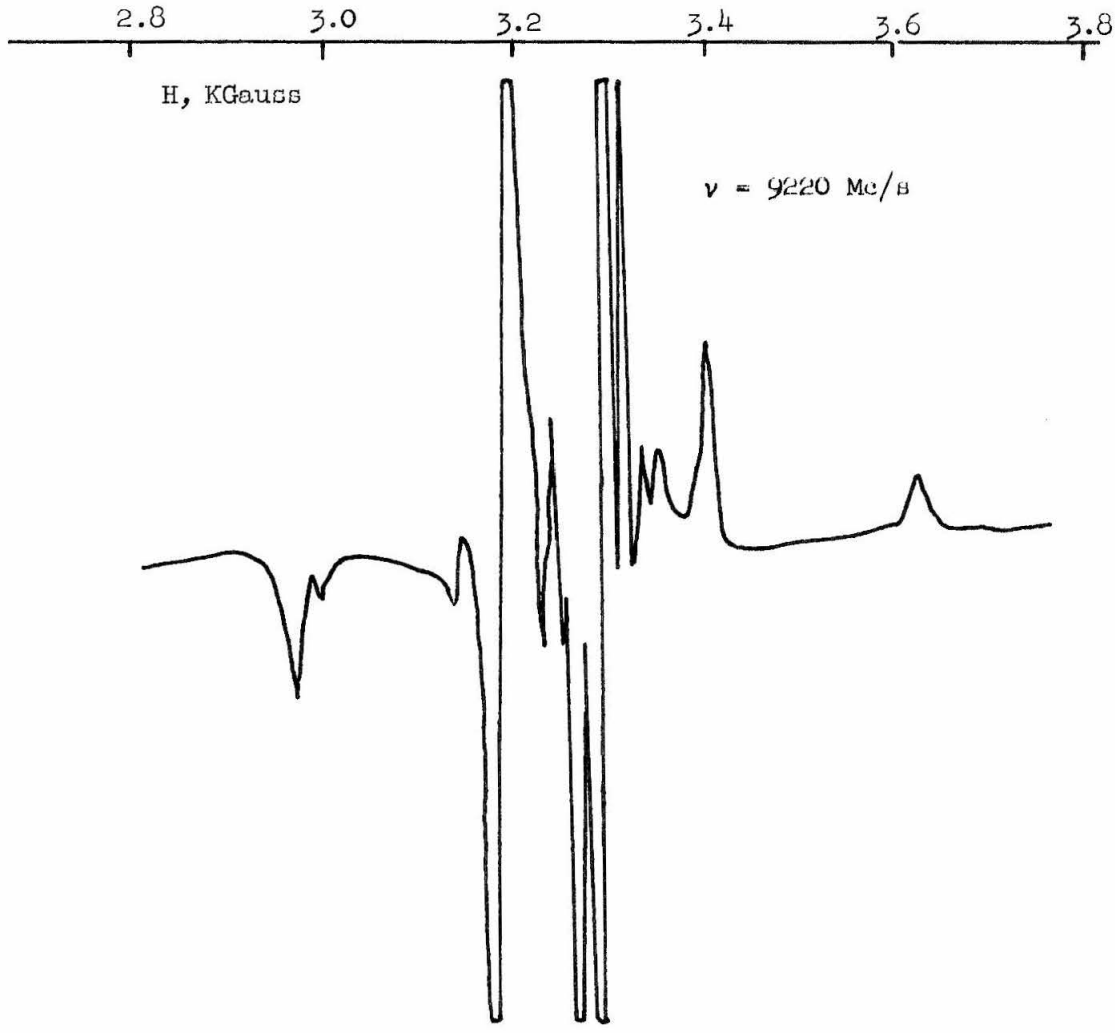


Figure 4. Esr spectrum of uv-irradiated $(C_6H_5)_3As$ in ethanol (96°K).

hyperfine splitting; in fact there appears to be no hyperfine splitting at all. This signal is shown on a more expanded scale in Figure 5. The shape of the signal looks like a typical three g-value pattern, with perhaps some unresolved arsenic hyperfine lending further asymmetry to the shape (82). It is very interesting that the rest of the spectrum looks so similar to that of diarsine. The fact that the region around $g = 2.07$ is rather different in the two cases, both in the hyperfine and in the symmetry of g seems to indicate that this signal is in each case due to the respective molecular cations. The similarity of the rest of the spectrum leads one to believe that there is a common product in the two cases. It is difficult to surmise what this "common product" might be. However, it is not unlikely that the two arsenic radicals $(CH_3)_2\ddot{A}s\cdot$ and $(C_6H_5)_2\ddot{A}s\cdot$ should have similar esr spectra. These might be expected to show sizable arsenic hyperfine splitting, by analogy with PH_2 ($\langle A_P \rangle = 80$ G.) (75).

It would obviously be of considerable help to have the esr spectra of these samples measured at a different magnetic field strength, in order to separate contributions from the electron-nuclear hyperfine interaction and the anistropy in the g-tensors. This experiment has been attempted, using the Varian K-band spectrometer. Satisfactory results have not been obtained however, due to technical difficulties. Part of the problem may be that it is necessary to carry out the irradiation externally and then rapidly transfer the sample into the sample cavity without thawing. A signal is obtained, but the level is too close to the noise level of the instrument to be of use.

The usual technique used to promote photooxidation is to carry

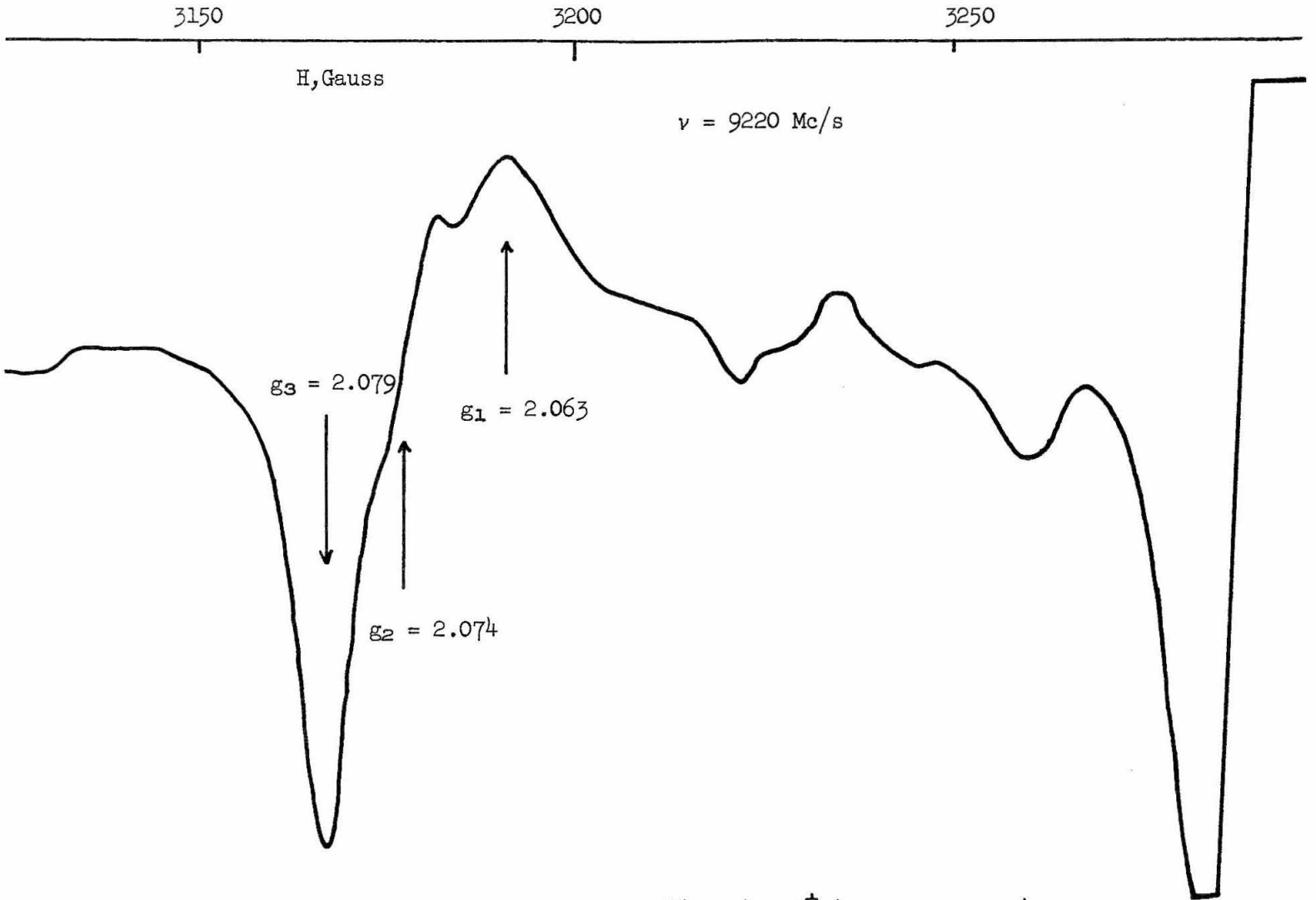


Figure 5. Esr spectrum of $[(C_6H_5)_3As]^+$ (expanded scale).

out the irradiation in a solution containing an electron acceptor (64), or in a medium which is itself a strong acceptor, such as concentrated sulfuric acid (83). Typical acceptor molecules often added to solutions for this purpose are carbon tetrachloride, benzyl chloride, benzoquinone, etc. All experiments using electron acceptors in solutions of these arsines have failed to give any of the normal arsine radical signals. Diarsine in sulfuric acid, or in solutions containing carbon tetrachloride, and triphenylarsine in ethanol with carbon tetrachloride or p-benzoquinone all give rise exclusively to signals in the vicinity of g = 2.00. The appearance of the signal observed with CCl_4 is quite similar to that obtained on warming the ordinary irradiated sample of diarsine enough to permit disappearance of the arsine radical signals.

A similar experiment was attempted beginning with the (diarsine·TCNE) charge-transfer complex in frozen solution. The electronic excitation which gives rise to the intense band in the spectrum of the molecular complex is described as a "charge-transfer" excitation, $(A \cdot D) \xrightarrow{h\nu} (A^-, D^+)^*$. For this reason, it was decided to irradiate the (diarsine·TCNE) complex with light of the same frequency as the charge-transfer transition in an attempt to produce the ($diars^+$,$TCNE^-$) ion pair. Irradiation at this wavelength (~ 500-700 nm) was found to give rise to no radical of any kind. Uv-irradiation generated the spectrum of $(TCNE)^-$ only. The same results were obtained using the (diarsine·chloranil) molecular complex.

From the experiments with charge-transfer complexes, it is clear that charge-transfer from diarsine to the electron acceptor does occur. This is also true when CCl_4 is used as the acceptor. In that case, no

signal appears on irradiation unless the arsine is added. The fact that no signals from arsine radicals are seen in these spectra must indicate that $(diars)^+$ and the other radicals produced react further with the electron acceptor, or radicals produced from it, to yield diamagnetic products. Another possible explanation is that the electron acceptor radical exhibits such an intense resonance that all other signals are simply buried. Because no signals from arsine radicals are observed, it might be concluded that diarsine does not act as an electron donor. The classical test for photooxidation is to add an acceptor to the sample and see whether the yield of radical cation increases. However, it seems quite likely that the cation radicals of the arsines are considerably more reactive than the amine radical cations on which the original work using electron acceptors was carried out. We conclude that the radical cation does form, that photooxidation of the arsine does occur.

Bis(diphenylarsino)ethane

The positions and shapes of all signals in the esr spectrum of this compound irradiated at 96°K in a 1:1 ethanol/toluene glass (Figure 6) are virtually indistinguishable from those of triphenylarsine (Figure 5). The only difference between the two cases is the ratio of peak heights of the two signals presumed to arise from different species. The signal at $g = 2.07$, corresponding to the molecular cation, and that at $g = 2.22$, corresponding to one component of the spectrum of R_2As. Complete results on this compound are listed in Tables VI and VII.

Dimethyliodoarsine

The esr spectrum of an ethanol solution of this compound uv-

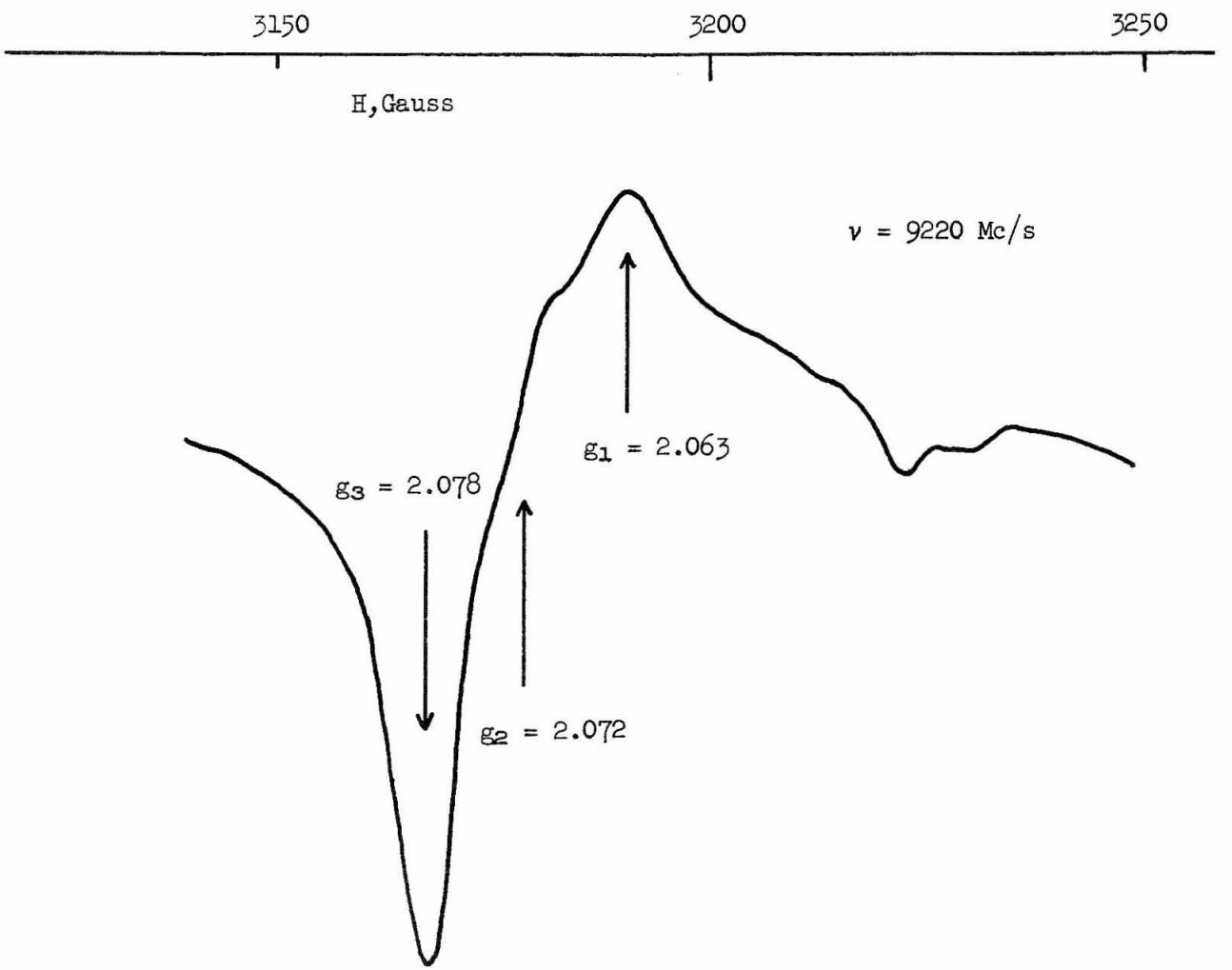
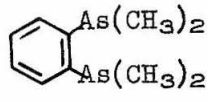


Figure 6. Esr spectrum of $[(C_6H_5)_2AsCH_2]^+$ (expanded scale).

Table VII

Peak Height Ratios

Compound	Peak ht. (g=2.075)/ Peak ht. (g=2.22)
$(C_6H_5)_3As$	15.6
$[(C_6H_5)_2AsCH_2]_2$	10.5
	5.05
$(CH_3)_2AsI$	2.85

irradiated at 96°K is pictured in Figure 7. The general features of the spectrum are the same as in all the other cases. The lines are considerably broadened here, and the peak height ratio represents an extreme. The peak height ratio data are set forth in Table VII, and provide evidence for the assignment presented above which identifies the signals at very high and low fields (including g = 2.22) with the fragment (R_2As). The ratio peak ht. g = 2.07/peak ht. g = 2.22 should increase with increasing stability of the molecular radical cation, and with increasing bond energy of the weakest bond to As. The stability of the radical cation is expected to increase with increasing phenyl-substitution. The As-I bond energy is low (D=49 kcal./mole) (31), and one expects extensive production of $(CH_3)_2As$ in the case of $(CH_3)_2AsI$. These expectations are borne out by the data in Table VII, in quite dramatic fashion. The proportion of molecular cation is greatest for triphenylarsine and least for dimethyliodoarsine, decreasing down the series by factors of two. While the peak height of the first derivative of the absorption signal is not strictly a measure of concentration, it suffices for this rather crude comparison.

Triphenylphosphine

Uv-irradiation of a solution of triphenylphosphine in ethanol at 96°K results in the slow appearance of the typical ethanol radical esr signal of five sharp lines. No other signal can be detected. The appearance of the five-line spectrum indicates that electron transfer must be occurring. Irradiation of ethanol alone gives a weak, asymmetric, one-line esr signal after very long irradiation times. It is clear that electron transfer involving the solvent is necessary to produce the

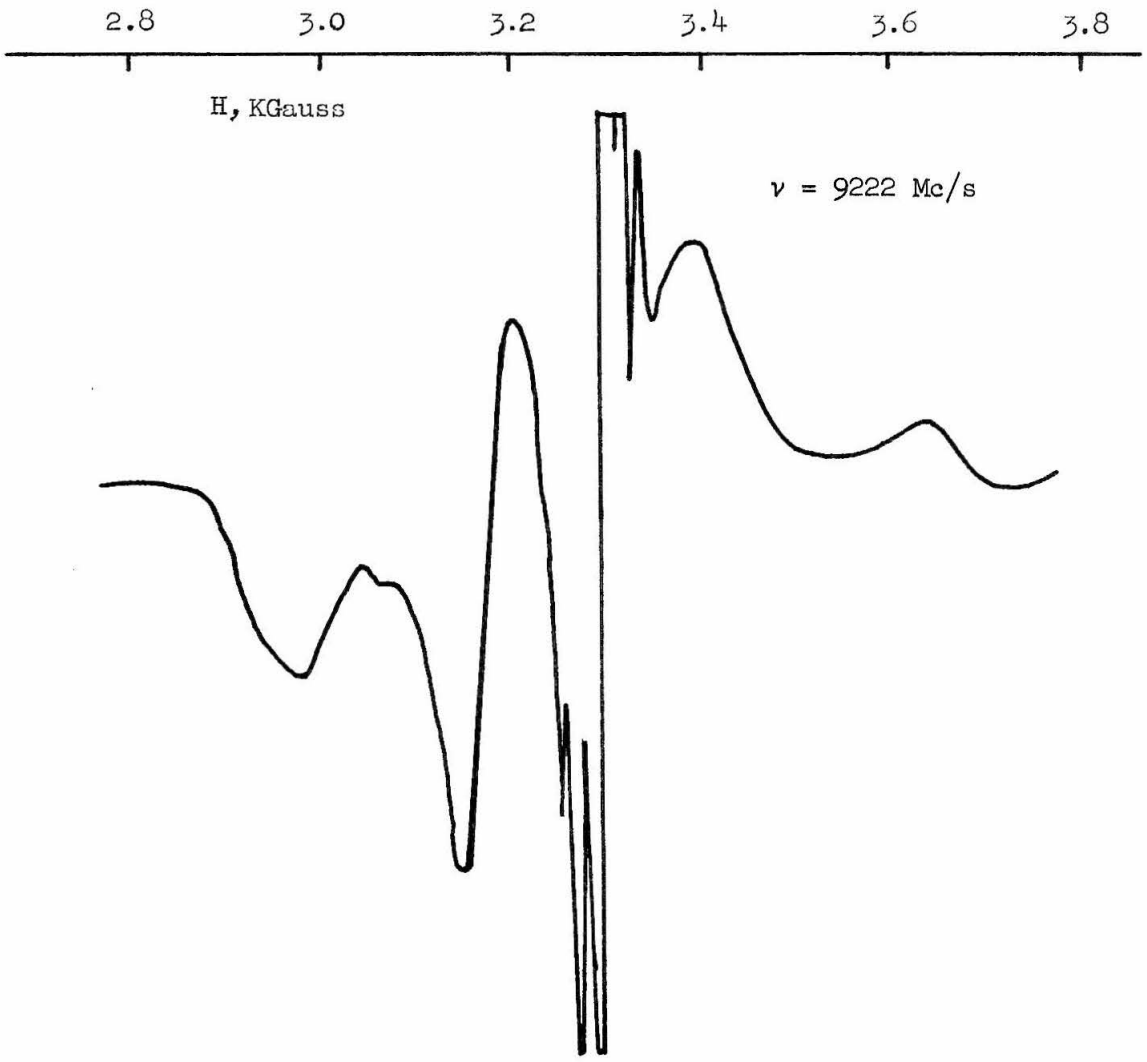


Figure 7. Esr spectrum of uv-irradiated $(CH_3)_2AsI$ in ethanol (96°K).

five-line spectrum. One expects to see a doublet from $[(C_6H_5)_3P]^+$, but none is observed. Most likely the signal is centered near g = 2.00 and is therefore buried under the signal from the solvent radical.

$[Ni(diars)_2Cl]^+$ and $[Ni(diars)_2Cl_2]^+$

It was mentioned earlier that the original intent of this study was to compare the esr spectrum of $(diars)^+$ with that obtained for the paramagnetic $Ni(diars)_2Cl_2^+$. When it was found that diarsine can apparently be photooxidized readily, efforts were made to photooxidize the five-coordinate d^8 complex, $Ni(diars)_2Cl^+$. This compound is very readily oxidized chemically (56). Uv-irradiation of a solution of $Ni(diars)_2Cl^+$ in ethanol at 98°K does not bring about oxidation. These solutions are usually contaminated with a small amount of paramagnetic $Ni(diars)_2Cl_2^+$ impurity, and the uv-irradiation brings about both a decrease in the esr signal due to this species, and appearance of the five-line ethanol radical spectrum. Thawing and mixing the solution, followed by remeasuring the spectrum at low temperature, shows a substantial decrease in the concentration of $Ni(diars)_2Cl_2^+$. The ethanol radical spectrum is also gone, of course. There is still another known oxidation state of the $[Ni(diars)X_2]^+$ complex, $Ni(diars)_2X_2^{2+}$, produced by oxidizing the $Ni(diars)_2X_2^+$ complex. This complex, formally nickel(IV), has an intense blue color (84). In order to determine whether reduction or oxidation of $Ni(diars)_2Cl_2^+$ occurs on uv-irradiation, a solution of $Ni(diars)_2Cl_2^+$ was irradiated at 96°K in the esr cavity. The orange color of the irradiated spot indicates that photoreduction to $Ni(diars)_2Cl^+$ is occurring. The charge-transfer process which occurs in this case must

then be

$$Ni(diars)_2Cl_2^+ + C_2H_5OH \rightarrow Ni(diars)_2Cl^+ + Cl^- + (C_2H_5\overset{+}{O}H)$$

$$(C_2H_5OH)^+ \rightarrow CH_3CHOH + H^+$$

It is interesting that the same stable radical is produced from ethanol independent of whether the initial charge-transfer product is $(C_2H_5OH)^+$ or $(C_2H_5OH)^-$. The mode of decomposition of these ions is expected to be determined by the stability of the products, and the secondary radical proposed is probably considerably more stable than the other possibilities.

Discussion

It would perhaps be of value to summarize briefly the proposed assignment of the esr spectra. In the spectrum of uv-irradiated diarsine, we assign the strong signal at $g = 2.075$, with the seven hyperfine lines, and the shoulder on the high-field side of this signal, to the species $(diars)^+$. This species seems to exhibit an axially symmetric g-tensor. The highly split pattern around $g = 2.00$ is assigned to one or more of the solvent radicals previously described. The other signals listed in Table VI are assigned to an arsenic-containing fragment, probably $(CH_3)_2As$. The spectra of the other uv-irradiated arsines are assigned in the same way. The only differences are, first, that $[(C_6H_5)_2AsCH_2]_2^+$ and $[(C_6H_5)_3As]^+$ appear to exhibit rhombic, rather than axially symmetric g-tensors, and second, that the other signals arising from arsenic radicals are assigned to $(C_6H_5)_2As$, which is expected to have an esr spectrum very similar to that of $(CH_3)_2As$. The assignment

of the esr spectrum of uv-irradiated dimethyliodoarsine is substantially the same as that of diarsine, with the exception that hyperfine splitting was not observed on the signal arising from the molecular cation.

The magnitude of the ^{75}As (I=3/2) hyperfine splitting observed for $(diars)^+$ is certainly quite small (a = 11.5 G.). Using the value of the isotropic arsenic hyperfine splitting arising from one unpaired 4s-electron, which has been calculated by Lin and McDowell (74), this 11.5 G. splitting implies that the unpaired electron in $(diars)^+$ possesses $\lesssim 0.3\%$ arsenic 4s-character. Hyperfine splitting is not observed in the other cases, and the linewidths of the signals due to $[(C_6H_5)_3As]^+$ and $[(C_6H_5)_2AsCH_2\frac{1}{2}]^+$ require that $\langle A_{As} \rangle \lesssim 5G$. Using the value of the ^{75}As anisotropic hyperfine splitting arising from one unpaired 4p-electron given by Lin and McDowell (74), we calculate that the unpaired spin in $(diars)^+$ has $\lesssim 5\%$ arsenic 4p-character. Since most of the unpaired spin density is neither in 4s or 4p orbitals of arsenic, there remain two reasonable possibilities, arsenic 4d orbitals and aromatic ring π-orbitals.

If we naively assume that the electronic structure of $(diars)^+$ can be obtained from that of diarsine by simply removing an electron from the highest occupied energy level of the latter, then assuming the energy level scheme described previously, the unpaired spin in the radical cation is expected to be localized in an MO consisting primarily of arsenic lone pair orbitals. The C–As–C bond angles in $(CH_3)_2As$ and $(C_6H_5)_3As$ are 96° (31), and the H–As–H angle in AsH_3 is 92° (85). This has been interpreted as indicating that the bonding orbitals in arsines involve arsenic orbitals which are essentially 4p-orbitals, and that the

lone pair is primarily of arsenic 4s character (85). It is quite clear that this can not be the case for $(diars)^+$. This problem was noted by Gordy, et al. in their esr study of PH_2 (75). They noted the discrepancy between the observed ^{31}P hyperfine splitting for that species and the prediction based on the above bond angle--sp hybridization model. They pointed out that d-orbital participation in the bonding would invalidate the relationships generally assumed (85) between bond angles and sp hybridization, and asserted that phosphorus 3d-orbitals should be involved in the bonding in PH_2. There is also microwave spectroscopic evidence for d-orbital participation in the bonding of H_2S (86) and AsH_3 (87).

Thus it appears quite reasonable that the orbital bearing the unpaired spin in $(diars)^+$ should possess some arsenic d-orbital character. Further evidence for d-orbital participation will be presented later. From the standpoint of energy, it seems unreasonable that the unpaired electron should be essentially an arsenic 4d electron, with small contributions from arsenic 4s and 4p orbitals. It is more likely that the aromatic ring π-orbitals are also significantly involved in the MO bearing the unpaired spin in $(diars)^+$. This interpretation is consistent with the observed hyperfine splitting in $(diars)^+$, and with the limit placed on $\langle A_{As} \rangle$ for the other radical cations studied. Similarly in the case of $[(CH_3)_2AsI]^+$, some delocalization of the unpaired spin into orbitals of the very polarizable I atom is expected.

The electronic spectral studies have indicated that there is little mixing between the heteroatom and aromatic orbitals, while the esr results reported here imply that there is mixing. Part of the problem stems from the fact that we are comparing electronic spectral results

on the neutral molecule with esr results on the cation. Since it is known that small changes in geometry can lead to important electronic structural changes in the molecules, such comparisons are of limited usefulness. It is also quite possible that the esr experiment is more sensitive than the electronic spectral measurement for detecting mixing of the arsenic and aromatic ring π-orbitals.

In order for the g-tensor to exhibit the observed anisotropy, arsenic d- or at least p-orbital contribution to the MO bearing the unpaired spin is required. Typical aliphatic and aromatic radicals containing only carbon, hydrogen, oxygen, and nitrogen all show g-values very close to 2.00 with almost no anisotropy (66). Spin-doublet transition metal ions, on the other hand, exhibit large anisotropies, e.g., for copper bis-acetylacetonate, $g_{\parallel} = 2.266$, $g_{\perp} = 2.053$ (88). Radicals containing sulfur and selenium have been found to exhibit anisotropies between these two extremes; for $\left(\mathrm{HOOC{-}\underset{\mathrm{NH_2}}{\underset{|}{CH}}{-}CH_2S\cdot}\right)$, $g_1 = 2.003$, $g_2 = 2.025$, $g_3 = 2.053$ (69). It appears that the arsenic-containing radical cations discussed here are similar to the latter case in the g anisotropy. Further experiments are necessary to completely establish the nature of the other arsenic signals present in the esr spectrum. Certain lines are observed which would correspond to g-values very far removed from the free-electron value if attributed to transitions involving no change in the nuclear spin state (g=2.22,g=1.83). It seems more likely that these lines correspond to hyperfine components which arise from splitting due to a single $^{75}As(I=3/2)$ nucleus. While the lineshapes tend to indicate that these signals correspond to radicals in different orientations with anisotropic g, the positions are split too widely from the free

electron value for this to be the complete explanation. We conclude that the observed extreme lines are components of ^{75}As hyperfine splitting. This leads to $\langle A_{As} \rangle \approx 150\text{-}220$ G. for R_2As, depending on the exact assignment.

The original purpose of this project was to obtain values for g's and $\langle A_{As} \rangle$ for $(diars)^+$ in order to compare these with the corresponding parameters derived from the esr spectra of $Ni(diars)_2Cl_2^+$ (see Table VIII). It is at once surprising that the value of $\langle A_{As} \rangle$ in the metal complex is greater than that observed in the diarsine radical cation (57). Apparently considerable rehybridization takes place in the arsenic orbitals upon complexing. It is also worth noting that the pattern of the g-values is different between the ligand radical cation and the paramagnetic complex. The g-tensor of the complex is rhombic, and that of the radical cation appears to be axially symmetric. It is certainly not true that the presence of the metal ion acts as a small perturbation on the electronic structure of the radical ligand. Whether the observed effect is primarily steric and geometric, as far as the unpaired spin is concerned, is difficult to know. This is probably not the case, however. It seems more likely that metal orbitals are strongly involved in the MO bearing the unpaired spin. This problem is being studied in some detail in a single-crystal esr study of $Ni(diars)_2Cl_2^+$ underway in these laboratories (58). The failure of uv-irradiation of $Ni(diars)_2Cl^+$ to produce any paramagnetic species is additional evidence against assigning the paramagnetic $Ni(diars)_2Cl_2^+$ as a metal-stabilized radical ligand. We know that uv-irradiation of diarsine readily produces the radical cation, and would expect a similar effect for the diamagnetic

Table VIII

Electron Spin Resonance Parameters of $(diars)^+$ and $Ni(diars)_2Cl_2^+$

$Ni(diars)_2Cl_2^+$ [a]	$diars^+$
$g_1 = 2.05$	$g = 2.041$
$g_2 = 2.09$	$g = 2.075$
$g_3 = 2.14$	
$\langle A_{As} \rangle = 23$ g.	$A_{As} = 11.5$ g.

[a] From Ref. 57.

nickel complex if this alluded-to description were correct. The presence of chloride in the sixth position may be very important to the stabilization of the paramagnetic species. Carrying out the irradiation experiment in concentrated chloride solution did not yield a different result, however.

We report the first preparation and characterization by esr of certain organoarsenic radicals. The esr results have been interpreted in terms of current notions concerning bonding and electronic structures in these compounds. The results indicate that in the aromatic arsine radical cations there is non-negligible mixing between the π-orbitals of the aromatic system and the heteroatom "lone pair" orbitals. Also, there appears to be evidence for Asd-orbital involvement in the bonding. A comparison of the esr results on $(diars)^+$ with those on $Ni(diars)_2Cl_2^+$ indicate that it is more appropriate to describe this metal complex in terms of delocalized MO's than as the d^8 metal ion with an oxidized radical ligand system.

II.

ELECTRONIC STRUCTURE OF FIVE-COORDINATE COMPLEXES OF LOW-SPIN NICKEL(II)

CHAPTER 1

INTRODUCTION: FIVE-COORDINATION

The traditional role which five-coordinate species have played in chemistry is that of the reaction intermediate or activated complex, a highly reactive species which rapidly proceeds to products. The five-coordinate intermediate (a species occupying a potential minimum) has been proposed for octahedral and square planar substitution reactions (89). A five-coordinate transition state (with which no potential minimum is associated) is believed to be involved in nucleophilic displacement reactions at tetrahedral carbon (90). Stable, five-coordinate compounds have been known for some time, but until recently, these were primarily limited to compounds of the Group V elements (91). In the past ten years, however, synthetic efforts in the area of five-coordination of transition metal complexes have been remarkably successful. A large number of five-coordinate transition metal complexes have been prepared and characterized, involving a rather wide variety of ligands and transition metal ions (91,92).

There are two alternative geometries in five-coordination, the trigonal bipyramid (TBP) and the square pyramid (SPY). Both of these, and a number of intermediate geometries are displayed by five-coordinate species. The question of what factors determine which of these geometries is assumed by a particular five-coordinate species has been of concern for some time (91). The actual situation is apparently that in

many cases the potential energy barrier between the two geometries is quite low, and so qualitative arguments about bonding preferences are in general too crude to be of help. The question of TBP versus SPY is very often based on quite subtle effects. Factors affecting five-coordinate geometry in transition metal complexes are perhaps more accessible than with the well-known Group V pentacoordinate molecules. In the former case there are a larger number of spectroscopic and magnetic techniques which can aid in elucidating the bonding in the different five-coordinate geometries. In any case, it is quite clear that there is great need for structural information about these complexes which can only be provided by X-ray diffraction techniques. Ibers and coworkers have recognized this need, and have already carried out a number of structure determinations of five-coordinate transition metal complexes (93).

In view of the relatively low barrier to interconversion between the two five-coordinate geometries, it is not surprising that the Group V halides and organic derivatives exhibit a considerable structural instability. Studies of ^{19}F nuclear magnetic resonance (nmr) show all fluorines equivalent in PF_5 at ambient temperature ($\sim$ 310°K). Measurements over a range of temperature confirm that rapid equilibration of the non-equivalent positions of the TBP is occurring (94). This process has been logically described as passing through an SPY transition state. This same type of scrambling has been observed for other Group V derivatives, and for iron pentacarbonyl (95). The matter of structural instability is of importance to the work reported here, and for this reason, it is perhaps well to look more closely at the factors which lead to

instability. This has been the subject of a certain amount of theoretical study recently. Eaton has shown how the Woodward-Hoffman rules can be modified to apply to transition metal complexes (96) and Pearson (97) has extended earlier work of Bader (98), which is based on the second-order Jahn-Teller effect, to analyze the same problem. Eaton's application of the Woodward-Hoffman rule to the problem of axial-equatorial exchange in the TBP shows that for the d^8 case, the exchange is expected to proceed readily through an SPY transition state. Pearson does not treat this case, but it is not difficult to show that the result predicted by the second-order Jahn-Teller effect is the same.

Taking into account the effect of a small distortion, the energy of a molecule may be expressed as (98)

$$E = E^{o} + \langle o|\frac{\partial V}{\partial Q}|o\rangle \; Q + \tfrac{1}{2} \; \langle o|\frac{\partial^2 V}{\partial Q^2}|o\rangle \; Q^2 + \sum_k \frac{|\langle o|\frac{\partial V}{\partial Q}|k\rangle|^2}{(E_o - E_k)} Q^2$$

The second term on the right-hand side of this equation corresponds to the first-order Jahn-Teller effect, and vanishes for a non-degenerate ground state. The third term is always nonzero and positive, corresponding to a simple Hooke's law-type potential which applies to any molecule undergoing a small distortion. The final term is always negative, and corresponds to the relaxation of the electronic distribution which occurs upon a small displacement of the nuclei. It is clear that if these last two terms are of comparable magnitude, a distortion of the molecule will occur with a very small activation energy. This situation can occur only when the matrix element $\langle o|\frac{\partial V}{\partial Q}|k\rangle$ does not vanish; that is, the direct product of the representations for the two molecular orbitals (MO's) in question must contain the representation of the dis-

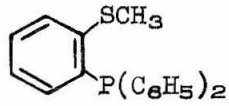
placement, Q. Bader has indicated that very often MO's other than the highest filled and the lowest unoccupied levels are too far apart in energy to give important contributions to the last term in (1). If $\Delta E \gtrsim 4$ eV, the contribution is likely to be too small (98). Pearson has stated the rule which can be derived from these considerations rather simply: "the symmetries of the ground electronic state and the lowest lying electronic state(s) determine which kind of nuclear displacement occurs most readily, i.e., the mode of decomposition or rearrangement of the molecule" (97). In the case of the transition metal TBP complex, the vibration which carried the molecule to the SPY geometry belongs to the E representation. The ground electronic state for the d^8 case is $^1A_1$ and the lowest excited state is ^1E, with a separation of $\sim$ 1.8-2.5 eV (8,17). Thus the TBP is expected to be unstable with respect to distortion towards the SPY geometry. The vibration which carries the SPY molecule to the TBP geometry is of B_1 symmetry (under C_{4v}). The ground electronic state for the d^8 case is $^1A_1$ and the first excited state is $^1B_1$, with a separation of $\sim$ 2.0 eV (99). This is also expected to be unstable. The instability of the five-coordinate geometries for the d^8 metal complex is thus readily understood using this interpretation.

We are interested here primarily in five-coordinate, low-spin d^8 metal complexes. Such complexes usually contain ligands with heavy donor atoms (S,Se,As,P) or strong π-acceptor ligands (CO, CN^-, CH_3NC). A few cases of five-coordination in this class involve monodentate ligands only. For these complexes, a common geometry is the distorted TBP (93, 100). It is not yet clear what properties of the ligand determine the

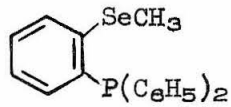
extent of distortion from the regular TBP. Jensen (101) has carried out synthetic studies on $Ni(TMP)_3X_2$ (X=Cl,Br,I,CN;TMP=trimethylphosphine) and Gray and coworkers have presented interpretations of the electronic absorption spectra of $Ni[(C_6H_5)P(OC_2H_5)_2]_3(CN)_2$ (25) and $Ni(TMP)_3Br_2$ (102).

A number of chelating ligands have been found particularly well-suited to the promotion of five-coordination in their metal complexes. Monodentate ligands in combination with bidentate chelating ligands often yield the SPY geometry, with the monodentate ligand providing an axial field and two bidentate ligands forming the square (or tetragonal) plane about the central metal atom (99,103). A number of the early cases of this geometry were prepared by Nyholm (99,104) using the ligand o-phenylenebisdimethylarsine (diarsine), with which he carried out a large number of other highly significant synthetic studies (2). These complexes involve gold (105) and the elements of the nickel triad (99) as central metal atom, and are of the form $[M(diars)_2X]^z$(M=Ni(II),Pd(II),Pt(II), Au(III);X=Cl,Br,I,NCS). The characterization and spectral measurements carried out on these complexes by Nyholm and coworkers will be further discussed later.

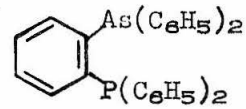
A number of five-coordinate, presumably square pyramidal complexes analogous to $Ni(diars)_2X^+$ have been prepared and characterized by Meek, et al. (106). These workers have used a number of ligands which are similar to diarsine, namely diphenyl(o-methylthiophenyl)phosphine (SP), diphenyl(o-methylselenophenyl)phosphine (SeP), diphenyl(o-diphenylarsinophenyl)phosphine (AP), and cis-1,2-bis(diphenylphosphine)ethylene (VPP).



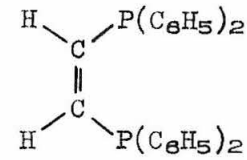
SP



SeP



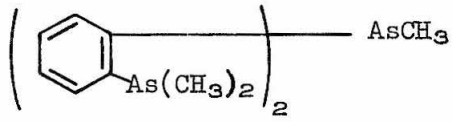
AP



VPP

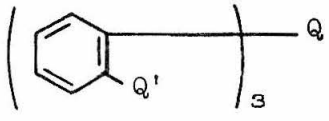
As well as the five-coordinate complexes of nickel(II), they have also prepared a number of five-coordinate complexes of cobalt(II) (107) and palladium(II) (9). The five-coordinate nickel complexes are again of the form NiL_2X^+, with X = Cl, Br, I, NCS, and conductance measurements were used to show that they are indeed five-coordinate. The electronic spectra of the complexes in dichloromethane solution have been reported, and show a striking similarity to those obtained for $Ni(diars)_2X^+$. On this basis we conclude that the structures of the two classes of complexes are the same. Because the spectra are different from those obtained for the known TBP complexes (108), the structure was tentatively assigned as SPY. More recently, a spectral comparison with a known SPY complex has confirmed this (106). We feel that the $Ni(diars)(trias)(ClO_4)_2$ electronic spectrum is rather similar to those obtained for $Ni(diars)_2X^+$ at low temperature. Since the structure of $Ni(diars)(trias)^{2+}$ (trias=bis(o-dimethylarsinophenyl)methylarsine) has been shown to be square pyramidal (109), we have assigned the same structure to $Ni(diars)_2X^+$, in accord with the original assignment of Nyholm (104). The spectra at room temperature are not so closely similar, and it would be useful to have a structure determination of one of the $(NiL_2X)ClO_4$ compounds as a reference point for the spectral work. Meek has presented an interpretation and assignment of the electronic spectra of a number of these complexes (106) which will be discussed later.

The terdentate ligands have been seen to give rise to SPY structures with two monodentate ligands or one bidentate ligand occupying the remaining two positions (21,110,111). One such terdentate ligand is triars, which forms the five-coordinate Ni(diars)(triars)$^{2+}$ (109).

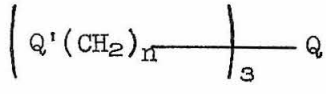


(triars)

Venanzi and coworkers (8), and subsequently Meek (17), Ciampolini (112) and others (113), have developed a type of tetradentate "tripod" ligand which effectively forces a trigonal bipyramidal geometry upon the metal atom, with a monodentate ligand (X) occupying the fifth (apical) position. This type of ligand has served as the basis for a prodigious amount of synthetic work. Eisenberg has recently summarized most of the known tripod ligands (114):



Q = P, Q' = $P(C_6H_5)_2$ (QP)
Q = As, Q' = $As(C_6H_5)_2$ (QAS)
Q = P, Q' = $S(CH_3)$ (TSP)
Q = As, Q' = $S(CH_3)$ (TSA)
Q = P, Q' = $Se(CH_3)$ (TSeP)



Q = As, Q' = $As(CH_3)_2$, n = 3 (TAA)
Q = P, Q' = $As(CH_3)_2$, n = 3 (TAP)
Q = N, Q' = $N(CH_3)_2$, n = 2 (Me_6 tren)

Both Venanzi and Meek have prepared and characterized many low-spin, d^8 TBP complexes of the type MLX^+ (where M =Ni,Pd,Pt;L=the tetradentate "tripod" ligand;X=halide,CN,CNS,etc.). In addition, both have measured

the electronic absorption spectra of these complexes, and presented interpretations of the ligand field bands (8,115). These will be discussed in some detail later.

CHAPTER 2

ELECTRONIC STRUCTURE IN FIVE-COORDINATION: TRIGONAL BIPYRAMIDAL COMPLEXES OF LOW-SPIN NICKEL(II)

Introduction

Since the preparation of the first complexes of the tetradentate "tripod" ligands (116-118), much work has been carried out on the preparation and characterization of this class of complex (8,17). Structure determinations on certain of the MLX^+ complexes have shown them to be trigonal bipyramidal, with the X group occupying an apical position trans to the odd donor atom of the tetradentate L group (114,119,120). The strong similarity of the ligand-field portion of the electronic spectra of all the low-spin d^8 (M=Ni(II),Pd(II),Pt(II)) MLX^+ complexes has led to the conclusion that all their structures are trigonal bipyramidal.

While considerable synthetic progress has been achieved using the "tripod" ligands, the measurement of electronic spectra has served primarily for the purpose of characterization. Such measurements have been limited to room temperature, and have been made mainly in the visible region. We have measured the spectra of these compounds in rigid glasses at 77°K, and have extended the measurements out to 41,000 $cm.^{-1}$. On the basis of these data, we present an electronic structural scheme for the complexes.

Experimental

All the metal complexes under investigation here are analyzed samples, kindly furnished by Professor Devon W. Meek of the Ohio State University. Solutions for spectral measurements were prepared using a 2:1 mixture of 2-methyltetrahydrofuran and ethanol or isopropyl alcohol. The isopropyl alcohol was spectroquality reagent (MCB), and the ethanol anhydrous U.S.P.-N.F. grade (U.S. Industrial Chemicals Co.). The 2-methyltetrahydrofuran was chromatoquality reagent (MCB) which was distilled from lithium aluminum hydride to remove peroxides and residual water. Spectral measurements were carried out as described previously.

Results

The visible absorption spectrum of $[Ni(TAA)Br]ClO_4$, representative of this class of complexes, is shown in Fig. 1. The spectrum of $[Ni(TAA)CN]ClO_4$ is displayed in Fig. 2. At low temperature, the broad asymmetric band exhibits a dramatic increase in extinction coefficient and becomes symmetric. Also, a much less intense band appears at somewhat higher energy. These results in part confirm the Gaussian analysis earlier performed on some of these spectra by Benner and Meek (17). Fig. 3 shows the ultraviolet (uv) absorption spectrum of $[Ni(TAA)Cl]ClO_4$. The considerably improved resolution at 77°K is characteristic of this region of the spectrum of these compounds. The complete results of the spectral study are set forth in Table I. Ligand abbreviations used in this section are as follows:

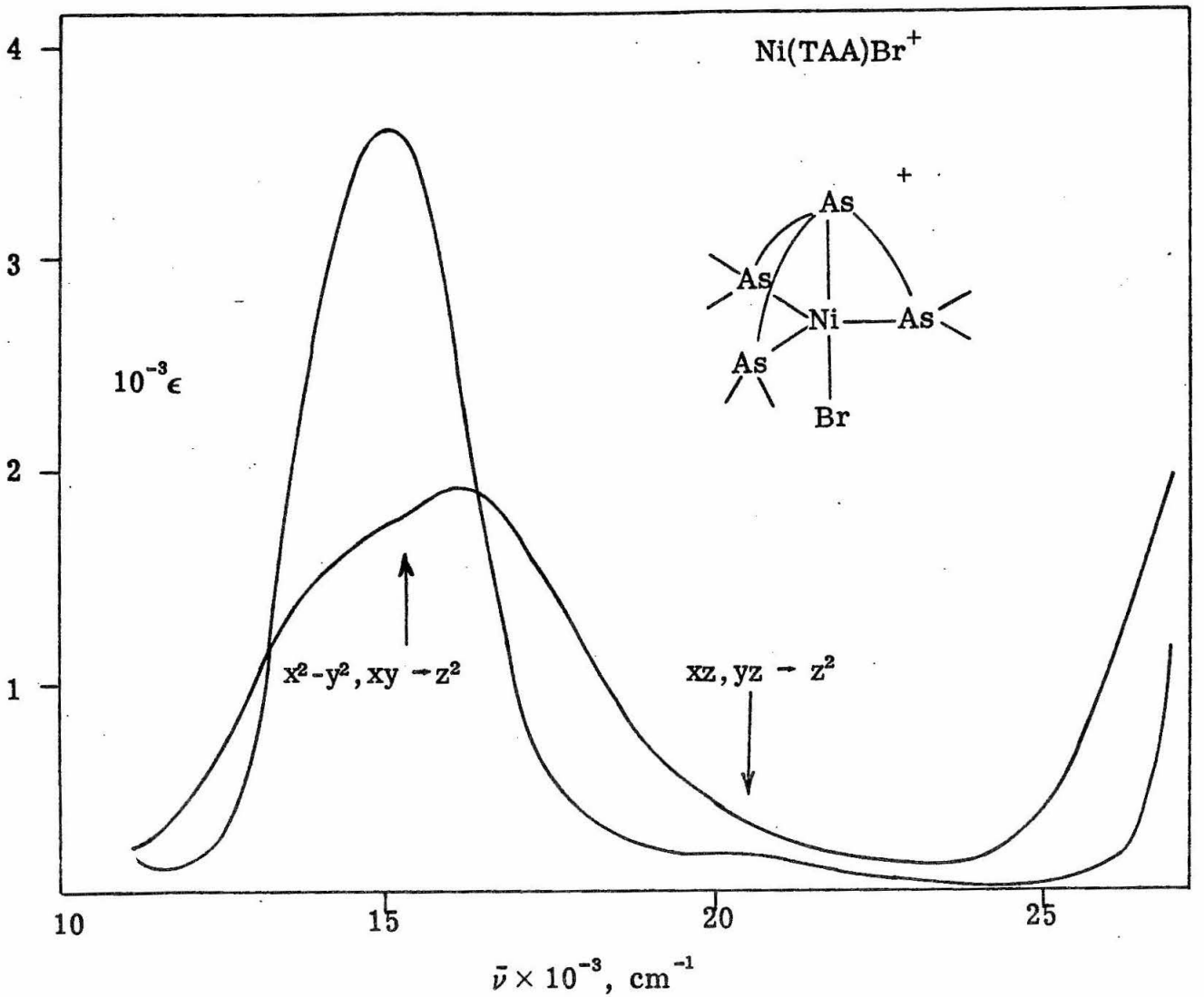

Ni(TAA)Br+
As
As
Ni
As
As
Br
+
10⁻³ϵ
x²-y², xy → z²
xz, yz → z²
4
3
2
1
10
15
20
25
ν̄ × 10⁻³, cm⁻¹

Figure 1

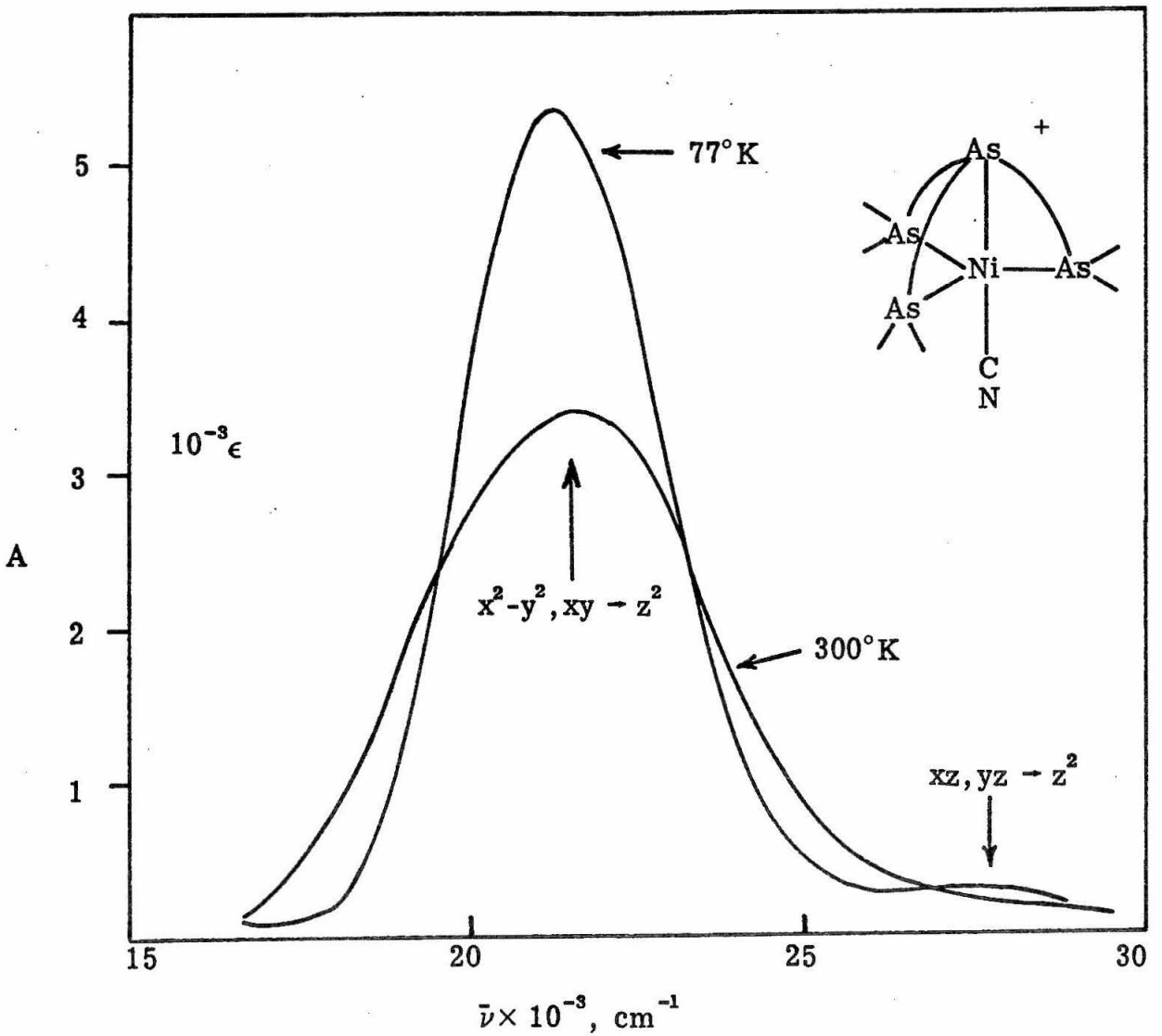

77°K
300°K
$10^{-3}\epsilon$
A
$x^2-y^2, xy \rightarrow z^2$
$xz, yz \rightarrow z^2$
As
As
Ni
As
As
C
N
+
5
4
3
2
1
15
20
25
30
$\bar{\nu} \times 10^{-3}$, cm^{-1}

Figure 2

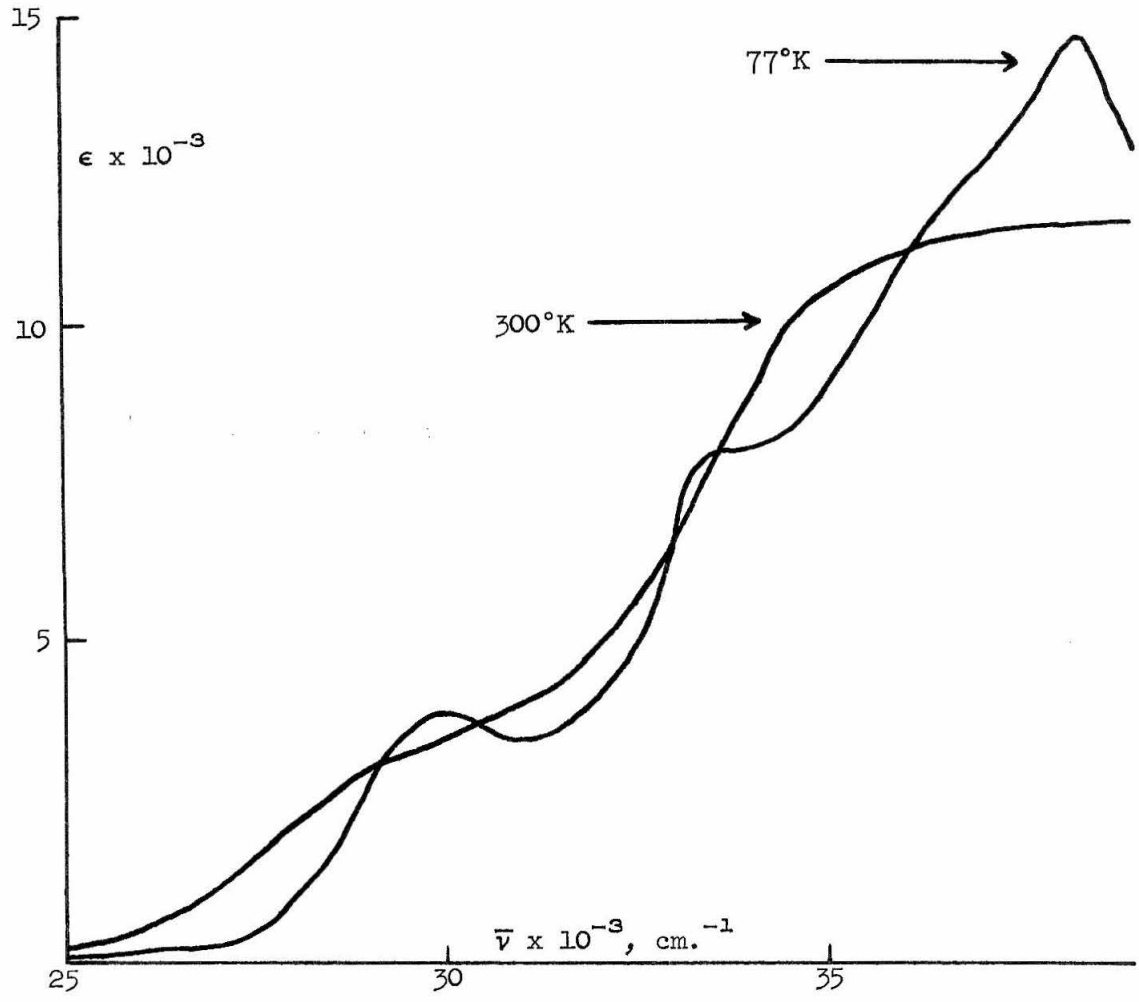


Figure 3. Electronic Spectrum of $[Ni(TAA)Cl]ClO_4$ in 2-methyltetrahydrofuran/ethanol (uv region).

Table I

Electronic Spectra of Trigonal-Bipyramidal Complexes at 77°K[a,b]

	[Ni(TAP)X]ClO$_4$				[Ni(TAA)X]ClO$_4$		
X =	Cl	Br	I	CN	Cl	Br	CN
$4e \rightarrow 4a_1$	16,880	16,190	15,620	22,860	15,600	15,100	21,230
$3e \rightarrow 4a_1$	22,470	22,220	21,740	29,410	20,790	19,800	27,625
$2e \rightarrow 4a_1$	31,600	29,940	27,210		30,000	28,600	
$1e \rightarrow 4a_1$	35,090	33,900	33,170		33,700	32,470	
$3a_1 \rightarrow 4a_1$	S37,740		S36,560		S36,800		
$2a_1 \rightarrow 4a_1$	39,220	38,170	37,520		38,300	37,240	
$4e \rightarrow CN(\pi^*)$				40,820			39,185

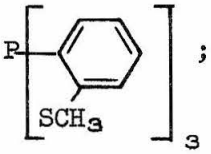
	[Ni(TSP)X]ClO$_4$				[Ni(TSeP)X]ClO$_4$		
X =	Br	I	NCS	Cl	Br	I	NCS
$4e \rightarrow 4a_1$	14,725	14,015	16,130	14,650	14,490	14,255	15,720
$3e \rightarrow 4a_1$	21,480	20,575	20,620	21,740	21,160	20,200	21,740
$2e \rightarrow 4a_1$	S29,630	26,540	S29,285	31,850	S29,200	S27,470	29,750
$1e \rightarrow 4a_1$	S32,735	S29,675	S33,335			29,370	
Ligand (internal)	S34,485	33,955	S34,720		S32,000	S32,100 (weak)	32,150
$2a_1 \rightarrow 4a_1$	38,460	S38,315	38,535	37,740	37,380	36,765	37,400
Ligand (internal)	S40,160	40,370	S39,920	40,400	40,400	40,570	41,200

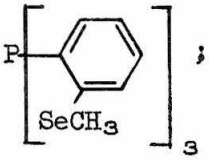
a-These results have been obtained in collaboration with Dr. J. E. Hix, Jr.

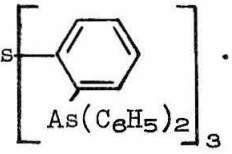
b-$\tilde{\nu}$ cm.$^{-1}$. Solvent 2:1 mixture of 2-methyltetrahydrofuran-ethanol. Selected extinction coefficients reported in Table VI.

TAA = As-[$CH_2CH_2CH_2As(CH_3)_2$]$_3$;

TAP = P-[$CH_2CH_2CH_2As(CH_3)_2$]$_3$;

TSP ≡  ;

TSeP ≡  ;

QAS ≡  .

The electronic structural scheme which has been used in assigning the spectral bands is similar to that given for $Ni(TMP)_3Br_2$ by Chastain, et al. (102). The ground state of $(NiLX)ClO_4$ is $\cdots (3e)^4(4e)^4 = {}^1A_1$.

A molecular orbital diagram for the TAA and TAP complexes is given in Figure 4. The ligand field levels are 3e, 4e, and $4a_1$.

The assignment of the ligand field spectrum presented here is in agreement with the principal features of the assignment given earlier by Venanzi, Meek, Ciampolini, and others for this type of complex (8, 115,121). The lowest energy band (ν_1), which is broad and asymmetric at room temperature, and which narrows and becomes more symmetric at 77°K, is assigned as the transition $4e \rightarrow 4a_1$ ($^1A_1 \rightarrow a^1E$). The band at higher energy (ν_2), which is considerably less intense, and which is well resolved at 77°K, is assigned as $3e \rightarrow 4a_1$ ($^1A_1 \rightarrow b^1E$). This intensity pattern has been observed for a large number of TBP complexes of both

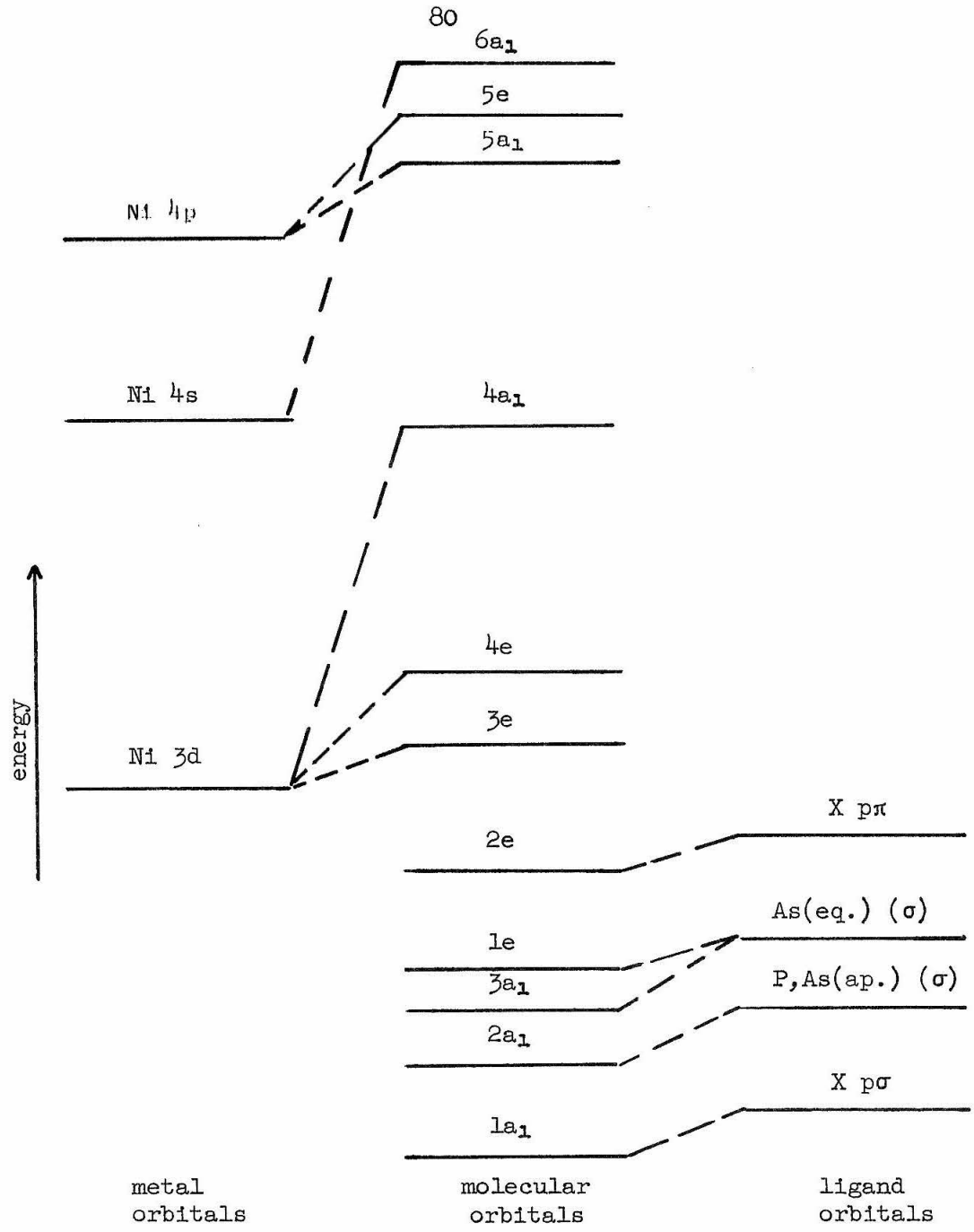


Figure 4. Relative molecular orbital energies for a trigonal bipyramidal $(C_{3v})NiLX^{+}$ (L=TAA or TAP;X=halide) complex. Only the principal correlation lines are shown.

D_{3h} and C_{3v} symmetry. Under D_{3h}, ν_1 is symmetry-allowed and ν_2 is symmetry-forbidden. Apparently lowering the symmetry from D_{3h} to C_{3v} does not have a marked effect on the intensity of ν_2, although the band does become formally symmetry-allowed.

There is a dramatic increase in the extinction coefficient of ν_1 on cooling to 77°K, as expected for a symmetry-allowed transition. Because ν_1 is far from Gaussian at room temperature, it is difficult to make an accurate measurement of the oscillator strength (f) of the band. Rough calculations indicate that the oscillator strength is independent of temperature, as it must be for a symmetry-allowed band (122). Because ν_2 appears as a weak shoulder on the high energy side of ν_1 at room temperature, it is not possible to tell how the oscillator strength of ν_2 depends on temperature.

While ν_1 does become more narrow and symmetrical at 77°K, the extent to which this occurs is dependent on X, the fifth ligand. Qualitatively, it appears that ν_1 becomes most symmetrical when X = CN and becomes progressively less so for Cl, Br, and I. It would be desirable to measure these spectra at lower temperatures to determine whether ν_1 becomes equally symmetric in every case, given sufficiently low temperatures. The change in appearance of ν_1 at low temperature is interpreted in terms of a model in which the geometry of the ground state is temperature-dependent in solution. This interpretation will be presented later in some detail.

The charge-transfer spectrum of the complexes of nickel(II) with TAA and TAP consists of three main bands. These fall in the regions 27,000-32,000 $cm.^{-1}$; 32,500-35,000 $cm.^{-1}$; and 37,000-39,500 $cm.^{-1}$ for the

complexes studied. Following Chastain, et al. (102), we have assumed the energy ordering $X(\pi) > As$, $P(\sigma) > X(\sigma)$ in assigning the spectral bands. The first charge-transfer band is assigned as $X(\pi) \rightarrow M(d\sigma^*)$, the second as As eq. $(\sigma) \rightarrow M(d\sigma^*)$, and the third as $P(\sigma)$ or As ap. $(\sigma) \rightarrow M(d\sigma^*)$. In some cases a shoulder appears between the second and third bands. This is assigned as a second component of the As eq. $(\sigma) \rightarrow Md(\sigma^*)$ transition (see Table I and Fig. 4).

Support for the assignment of the first charge-transfer band as $X(\pi) \rightarrow M(d\sigma^*)$ is provided by the substantial variation in the band position on changing X. The position varies in the predicted order for an $X(\pi) \rightarrow M(d\sigma^*)$ charge-transfer band, $I < Br < Cl$ (26). Assignment of the other two charge-transfer bands has been carried out in conjunction with results from the TSP and TSeP complexes. The charge-transfer spectra of the TSP and TSeP complexes again exhibit three main bands. They fall in the regions 26,500-32,000 $cm.^{-1}$; 29,000-33,500 $cm.^{-1}$; and 36,500-38,500 $cm.^{-1}$. There is apparently some interference in the ultraviolet region by internal ligand absorption, as indicated in Table I. The lowest energy charge-transfer band in $Ni(TSP)X^+$ and $Ni(TSeP)X^+$ is very close in energy to that in $Ni(TAP)X^+$, and again the energy of the band varies in the order $Cl > Br > I$. This band is therefore assigned as $X(\pi) \rightarrow M(d\sigma^*)$. With the exception of the two cyanide complexes, every compound studied exhibits an intense charge-transfer band in the region 36,500-39,500 $cm.^{-1}$. This band remains of approximately constant shape throughout the series of compounds, and varies in position about as much as the first ligand field band (ν_1). This intense charge-transfer transition is assigned as $P(\sigma) \rightarrow M(d\sigma^*)$ for the TAP, TSP, and TSeP complexes,

and as As ap. (σ) → M($d\sigma^*$) for the TAA complexes. The intermediate charge-transfer band (29,000-35,000 cm.$^{-1}$) varies considerably in shape and position in the series of complexes, and is assigned as the allowed component of As(σ) → M($d\sigma^*$) in the TAP complexes, As eq. (σ) → M($d\sigma^*$) in the TAA complexes, and S,Se(π) → M($d\sigma^*$) in the TSP and TSeP complexes.

It is not possible to measure beyond 41,000 cm.$^{-1}$ with this solvent, and so the X(σ) → M($d\sigma^*$) band is not observed. This band would be expected in the region 36,000-48,000 cm.$^{-1}$ for the various complexes included, because it appears to be true that Δ [X(π) - X(σ)] ≈ 10,000-16,000 cm.$^{-1}$ (as determined spectrally) for a number of complexes (26). It is also expected that the S,Se(σ) → M($d\sigma^*$) transition should occur at energies greater than 41,000 cm.$^{-1}$.

Discussion

The spectral results reported here are in substantial agreement with the original studies of these compounds made by Meek and coworkers (17). We have extended this earlier work by carrying out the electronic spectral measurements at 77°K in glassy, frozen solutions. The spectrochemical series ordering which was earlier reported by Veranzi and Meek for TBP complexes containing the "tripod" ligands is maintained in the low temperature spectra reported here. Both ligand-field bands exhibit the energy ordering, CN > NCS > Cl > Br > I. Also, upon changing the tripod ligand, the ordering is P > As > S > Se (115).

A qualitative molecular orbital (MO) scheme for these complexes is given in Fig. 4. The $4a_1(z^2)$ level is the highest of the ligand field levels, and is unoccupied. This orbital is destabilized by axial σ-bond-

ing. Thus in the absence of changes in the geometry of the $(NiL)^{2+}$ unit, the σ-donor ability of the X group is expected to determine the extent of destabilization experienced by this MO. This destabilization should in turn be reflected in the position of the lowest energy ligand field band (ν_1), because the level from which this transition originates is $^4e(x^2-y^2,xy)$. As a first approximation, the energy of the ^4e level should be independent of X. The measured values of ν_1 (see Table 1) seem to bear this out. In the case of the SPY complexes of the type $[Ni(diars)_2X]^Z$, it will be seen that a very definite effect on those ligand field levels involved only in interactions with the arsenic donor atom framework is observed when X is changed. This effect is discussed in some detail in Chapter 3. Briefly, the crucial factor in this divergence of behavior is thought to be the occupied or unoccupied nature of the dz^2 orbital in the complex.

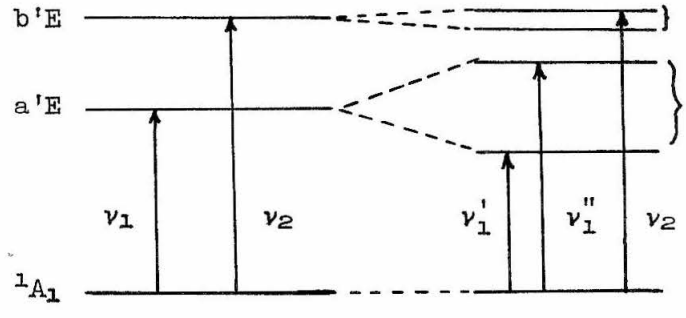
The lowest energy ligand field level for the TBP complexes is $^3e(xz,yz)$, which includes contributions from X(π) orbitals. It is destabilized by π-donor ligands and stabilized by π-acceptors. This effect can be detected in the second ligand field band. Assuming that the energy of the $^4e(x^2-y^2,xy)$ level does not depend upon the nature of X, the relative positions of the $^4a_1(z^2)$ levels in two $[NiLX^+]$ complexes is given by the difference in position of ν_1 for the two species. Since this assumption is not strictly correct, we choose an illustrative example with a large difference in ν_1, the two complexes $[Ni(TAA)CN^+]$ and $[Ni(TAA)Cl^+]$. The differences in ν_1 and ν_2 between the different halide derivatives are so small that a comparison of two halide complexes is not meaningful.

Using the data in Table I, and neglecting interelectronic repulsion effects, we estimate the $4a_1(z^2)$ level in Ni(TAA)CN^+ to be above the corresponding level is Ni(TAA)Cl^+ by 5630 cm.$^{-1}$. The value of ν_2 yields, again neglecting the effect of interelectronic repulsion, the approximate separation between the $4a_1(z^2)$ level and the $3e(xz,yz)$ level. We can use the values of ν_2 for the complexes under consideration in conjunction with the separation between the two $4a_1$ levels calculated above to determine the relative positions of the $3e$ levels in the two complexes. The difference in ν_2 between Ni(TAA)CN^+ and Ni(TAA)Cl^+ is 6835 cm.$^{-1}$. The $4a_1$ level in the cyanide is above that in the chloride by 5630 cm.$^{-1}$, therefore the $3e$ level in the cyanide must be significantly below that in the chloride. We would calculate a difference of 1205 cm.$^{-1}$ between the two $3e$ levels; the actual value is not of great significance. The point is that the $3e$ level of the cyanide is found experimentally to be below that of the chloride. Since chloride is a π-donor ligand and cyanide is a good π-acceptor, a qualitative MO interpretation would predict this experimental result correctly. This simple calculation can be repeated to compare the cyanide derivatives with any of the other corresponding halides (see Table I), and the same result is obtained. In comparing the halides with one another, the separations involved are too small, and the results do not fit any self-consistent pattern.

It was anticipated that a study of the electronic spectra of these compounds at low temperature would provide a means for checking the Gaussian analysis of the room temperature spectra performed by Benner and Meek (17). In fact, the higher energy ligand field band (ν_2) was well resolved at low temperature, and its position at 77°K is in reason-

able agreement with the band calculated in the Gaussian analysis. The behavior of the lower energy ligand field band (ν_1) upon cooling has been described. This band is asymmetric at room temperature, and Gaussian analysis gives a good fit assuming two bands (17). The two component bands are not resolved at 77°K. Instead, ν_1 is considerably more symmetrical at low temperature.

The asymmetric shape of ν_1 in the very similar $M(QAS)X^+$(M=Pd,Pt; X=Cl,Br,I,SCN) was attributed by Venanzi (8) to a static distortion of the trigonal plane of arsenic atoms about the central metal. He cited as evidence the results of a structure determination on $Pt(QAS)I^+$ (119), which was found to be a slightly distorted TBP. This distortion destroys the three-fold rotation axis of the molecule, and thus lifts the degeneracy of all electronic states which were degenerate under C_{3v}. The new molecular symmetry is C_s. The effect of the distortion on the lowest energy electronic states of the molecule is pictured below. The discussion which follows is directly applicable to molecules possessing D_{3h} symmetry, by simply substituting the symmetry designations D_{3h} and C_{2v} for C_{3v} and C_s.



C_{3v} (regular TBP) C_s (distorted TBP)

Figure 5

There is no way of knowing à priori whether the splitting of energy levels brought about by a molecular distortion will be observable as a splitting in a spectral band. The fact that ν_1 exhibits the splitting and ν_2 does not simply indicates that the dependence of energy level splitting on molecular distortion is much pronounced for a^1E than for b^1E.

Ibers and coworkers have recently reported the determination of the crystal and molecular structures of the five-coordinate species $Ni[(C_6H_5)P(CH_3)_2]_3(CN)_2$ and $Ni[(C_6H_5)P(OC_2H_5)_2]_3(CN)_2$ (93,123). Their results show that $Ni[(C_6H_5)P(OC_2H_5)_2]_3(CN)_2$ exhibits considerably more distortion from D_{3h} symmetry than does $Ni[(C_6H_5)P(CH_3)_2]_3(CN)_2$. Recent electronic spectral studies in our laboratories have shown that the splitting of ν_1 in the room temperature solution spectrum correlates with the extent of distortion in these complexes (124).

	$(\nu_1'' - \nu_1')$	Molecular Symmetry
$Ni[(C_6H_5)P(CH_3)_2]_3(CN)_2$	2400 $cm.^{-1}$	D_{3h} (slightly distorted)
$Ni[(C_6H_5)P(OC_2H_5)_2]_3(CN)_2$	3400	C_{2v}

The spectrum of $Ni[(C_6H_5)P(OC_2H_5)_2]_3(CN)_2$ at 77°K in a rigid glass, at room temperature in solution, and at intermediate temperatures is pictured in Figure 6. This compound shows the most dramatic temperature dependence of the splitting of ν_1 yet observed (124).

It has also been found that the electronic spectrum of $Fe(CO)_5$ in solution shows very little change in passing from room temperature to 77°K. ν_1 is quite symmetrical at both temperatures (125). This observation is in accord with the regular TBP structure of this species as

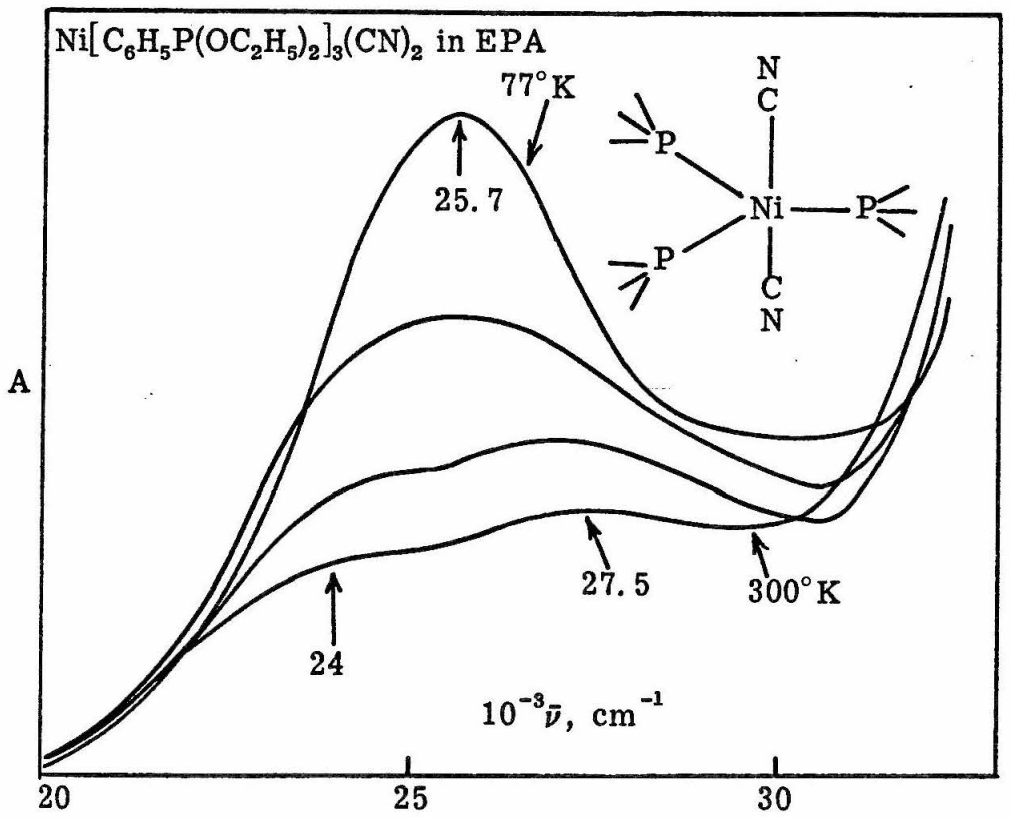

Ni[C6H5P(OC2H5)2]3(CN)2 in EPA
77°K
25.7
N
C
P
Ni
P
P
P
C
N
A
27.5
300°K
24
10^-3 ν̄, cm^-1
20
25
30

Figure 6

determined by X-ray diffraction techniques (126). Structure determinations on TBP complexes of the "tripod" ligands have all revealed them to be slightly distorted (114,119,120). Likewise, ν_1 is asymmetric in the room temperature solution spectrum for all the metal-"tripod" complexes studied here.

If the distorted structure is maintained at low temperature, however, the two components of the asymmetric band are expected to be resolved. Since this does not occur, and the band in fact becomes more symmetrical, there must be a difference in structure between the complex in solution at 77°K and in the solid at room temperature. In particular, the complex must be in the regular TBP form (C_{3v}) at low temperature in solution, for only in this way will ν_1 be unsplit.

This explanation suggests that it may be reasonable to analyze this problem in terms of an equilibrium between the two forms. This model is analogous to the "spin-equilibrium" reported in ferric dithiocarbamate (127), and the four-coordinate/five-coordinate equilibrium observed for $Ni(Et_4dien)X_2$ (5) (Et_4 dien=1,1,7,7-tetraethyldiethylenetriamine;X=Cl,Br,I).

$$\text{(Regular TBP) } C_{3v} \rightleftharpoons^{K} C_s \text{ (Distorted TBP)}$$

We designate the two forms by their point groups. On the basis of this model, it is required that at intermediate temperatures an equilibrium mixture of the two forms be maintained. Referring to Figure 5, it is noted that an equilibrium mixture of the C_{3v} and C_s forms is expected to show three spectral bands in the region of ν_1.

We have observed spectra in which ν_1 had begun to become symmetrical upon cooling, but had not become completely symmetrical. Under these

conditions, the model predicts an equilibrium mixture of the C_s and C_{3v} forms. Two examples of this observed behavior are the $Ni(TAA)Br^+$, for which ν_1 is not completely symmetrical at 77°K but is considerably more so than at 300°K, and $Ni[(C_6H_5)P(OC_2H_5)_2]_3(CN)_2$, which has been studied at temperatures between 77° and 300°K (124). However, in no case has it been possible to observe more than two spectral bands. It is true that the energy separations between ν_1, ν_1', and ν_1'' are relatively small for these complexes, and that three overlapping bands might appear to be only two. It is thus not possible to rule out completely an equilibrium on the basis of the available data.

The absence of any experimental evidence for an equilibrium involving two distinct components has led us to consider the possibility that species of intermediate geometry are present at intermediate temperatures. It is likely that the energy difference between the two "limiting" structures, C_s and C_{3v}, is rather small, and that in condensed phases, solvent-solute interactions, for example, will be large enough to alter significantly the shape and the equilibrium position of the ground state potential function. Thus it appears that a variety of stable structures with differing degrees of distortion could exist, and that the actual geometry of the species present would be a function of temperature. This model involving the existence of structures with intermediate geometry at intermediate temperatures would lead to the observed spectroscopic behavior. Under this model, the species present at any given temperature would be the intermediate structure most stable at that temperature, rather than some mixture of only the C_{3v} and "limiting" C_s forms. Thus the appearance of ν_1 should reflect the amount of

distortion in this intermediate structure, rather than being simply the superposition of bands due to the C_{3v} and "limiting" C_s forms.

On the basis of this explanation, it is interesting to speculate on the nature of the structure which would be stable in the absence of intermolecular interactions. Because the regular C_{3v} form is favored at low temperature, it appears that in the gas phase, for example, these molecules should be regular. In condensed phases, intermolecular interactions tend to distort these "configurationally unstable" structures. In the low-temperature glass, the five-coordinate complex adopts the regular structure (C_{3v}) because of the reduction in the solvent-solute interaction. This interaction is reduced because of the large increase in the solvent-solvent interaction which occurs in glass formation.

The phenomenon which has been described here is not commonly observed in electronic absorption spectroscopy. In fact, we do not know of any previous report of this type of temperature dependence of spectral bands. In view of this, one must consider why this system, in particular, should exhibit the observed effect. One obvious necessity is the presence of a low-lying, degenerate excited electronic state and a non-degenerate ground state. A very important additional feature appears to be the possibility of having either the regular structure, or distorted structures in which the degeneracy of the low-lying excited state is removed. Finally, the dependence of the splitting of the degenerate state on the amount of distortion must be dramatic enough to be observable.

The apparent requirement for an accessible distorted structure(s)

may explain why this effect has not been seen in the octahedral, tetrahedral, or square planar cases. Both Eaton and Pearson have shown that the tetrahedral structure is not expected to exhibit structural instability towards the square planar for any of the possible electronic configurations with orbitally non-degenerate ground states (96,97). The octahedral structure is not expected to show instability with respect to the trigonal prism, because the nuclear motion relating the two structures is not a normal mode for the octahedron. One might hope to observe the effect described here in eight-coordination, where the dodecahedron and square antiprism are geometries of similar energy. Another possible system is the distorted octahedral tris-complex of the dithiolene-type ligands with some of the early first-row transition metals (128).

CHAPTER 3

ELECTRONIC STRUCTURE IN FIVE-COORDINATION: SQUARE PYRAMIDAL COMPLEXES OF NICKEL(II) WITH o-PHENYLENEBISDIMETHYLARSINE

Introduction

It has been known for some time that the bis-diarsine complexes of M(II) (M=Ni,Pd,Pt) readily form adducts of higher coordination number with various simple ligands (X) (99,104).

The pioneering work of Nyholm on the transition metal complexes of diarsine included conductivity and spectrophotometric evidence which indicated that these adducts are five-coordinate in solution. Since that time, additional evidence has been provided by Peloso and coworkers, who were able to determine formation constants and thermodynamic parameters for a wide range of the $[M(diars)_2X]^Z$(M=Ni(II),Pd(II),Pt(II)) species (129). Speculation concerning the structure of these five-coordinate complexes has centered about a square pyramidal model (104). Also, crystal and molecular structure of the once very puzzling compound (130) now known to be $Ni(diars)(triars)(ClO_4)_2$ has been determined (109). The complex ion is composed of a nearly regular square pyramid of As atoms about the central nickel atom. It appears that the five-coordinate complexes of nickel(II) with diarsine may be a good system in which to study the electronic structure of the low-spin square pyramidal complex. Although a significant number of low-spin d^8 square pyramidal structures have been determined by X-ray methods (91,100,111), and some electronic spectra have been measured, there has been little discussion of the

detailed electronic structure for this case.

We have measured the electronic absorption spectra of a series of the five-coordinate complexes of the type $[Ni(diars)_2X]^z$, and the four-coordinate species $[Ni(diars)_2]^{2+}$ in solution at 300°K and in frozen solutions which form a clear, rigid glass at 77°K. The increased resolution achieved at low temperature has proved very important in facilitating assignment of the ligand-field spectrum. The temperature-dependence of the spectra also furnishes evidence concerning the symmetry-allowed or -forbidden character of the bands. The spectral results are discussed in terms of a qualitative molecular orbital scheme to these complexes.

Experimental

Preparation of Compounds

Reagents. All metal salts were reagent grade and were used without further purification. The ligand o-phenylenebisdimethylarsine (diarsine) was prepared and purified as previously described.

$Ni(diars)_2X_2$ (X=Cl,Br,I) was prepared according to the method of Nyholm (56) and recrystallized for ethanol. $Ni(diars)_2(ClO_4)_2$ was prepared by the method of Harris, et al. (99) and recrystallized from a mixture of acetonitrile and ethanol. $Ni(diars)(triars)(ClO_4)_2$ was prepared using the nickel(II) catalyzed conversion of diars to triars described by Nyholm, et al. (109,130). All samples were analyzed for C, H, and As (Galbraith Microanalytical Laboratory, Knoxville, Tenn.) and characterized by the visible absorption spectra.

$[Ni(diars)_2X]ClO_4$ (X=Cl,Br,I,NCS,NO_2). These compounds were prepared by a modification of Nyholm's method (99). This modification was suggested by the method used by Meek and coworkers (17) to prepare complexes of the type $[NiLX]ClO_4$ where L = a tetradentate "tripod" ligand and X = Cl, Br, I, CN, NCS. The method consists of mixing equimolar amounts of $Ni(ClO_4)_2 \cdot 6H_2O$ and NiX_2 in ethanol and adding a stoichiometric amount of diarsine in ethanol to produce the solid $[Ni(diars)_2X]ClO_4$. The product was recrystallized from dichloromethane or methanol. All samples were analyzed for C, H, and A_s, and the results found to be in excellent agreement with theory.

$[Ni(diars)_2CN]ClO_4$. This compound was first prepared in an unusual reaction involving $Ni(diars)_2(ClO_4)_2$ and tetracyanoethylene (TCNE) in ethanol. $Ni(diars)_2(ClO_4)_2$ (.035 gm.) was mixed with ethanol (35 ml.), in which it is very slightly soluble, and TCNE (.035 gm.) was added. Upon heating on the steam bath, a red solution was formed. The solution was filtered, and upon reducing the volume of solution or addition of ethyl ether, a red solid precipitated. This material was impure, but recrystallization from methanol afforded dark red crystals of the compound. This compound can probably also be prepared directly from $Ni(CN)_2 \cdot 4H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, and diarsine, by the method described previously. The solid exhibits a single, sharp C-N stretching frequency at 2101 $cm.^{-1}$. In acetonitrile it appears at 2109 $cm.^{-1}$.

Anal. Calcd. for $[Ni(diars)_2CN]ClO_4$: C, 33.35; H, 4.26; As, 39.62.

Found: C, 33.31; H, 4.35; As, 39.34.

$Ni(diars)_2(thiourea)(ClO_4)_2$. $Ni(diars)_2(ClO_4)_2$ was mixed with ethanol containing a large excess of thiourea. A red solid was formed

after warming a few minutes on the steam bath. The solid was filtered off and washed repeatedly with cold ethanol, in which it was sparingly soluble. This complex is extensively dissociated in ethanol solution to $Ni(diars)_2^{2+}$ + thiourea. Addition of an excess of thiourea to the ethanol solution is necessary to suppress dissociation.

Anal. Calcd. for $[Ni(diars)_2(thiourea)](ClO_4)_2$: C, 27.84; H, 4.01; As, 33.08.

Found: C, 27.74; H, 3.93; As, 33.33.

Physical Measurements

All ultraviolet and visible spectral measurements were made on the Cary Model 14RI spectrophotometer. Measurement of spectra at 77°K were carried out as previously described. Measurements in the visible region were made using pyrex square cells prepared from square tubing obtained from Wilmad Glass Co. For the ultraviolet region, quartz cells of a similar type were used. In this case, however, the cells were made by molding round quartz tubing on a square, solid molybdenum form. The advantage of these cells over fused or cemeted quartz square cells is that they show much less tendency to induce crack formation in unstable rigid glasses at 77°K. A number of the measurements were carried out using commercial Suprasil square cells, and these results agree well with those taken using the tubing cells (62). Repeated measurements have been carried out using these cells, and reproducibility is good. Baseline measurements using solvent alone at 300°K and 77°K were used to correct measured spectra. Solutions for spectral measurements were prepared using the 2:1 mixture of 2-methyltetrahydrofuran and methanol, propionitrile, or ethanol described earlier. A 2:1 mixture of

of ethanol and ethyl ether was found to form a transparent, uncracked glass on a certain percentage of tries, and this was used for a number of measurements. Propionitrile (Eastman white label) was purified according to a published method (132).

Molar extinction coefficients at 77°K have been corrected for volume contraction using correction factors given earlier. The contraction of the 2:1 ethanol-ethyl ether mixture at 77°K is 20%, as determined by cooling a measured volume of solvent in a graduated tube.

Infrared spectra of Nujol mulls were measured on a Perkin-Elmer Model 225 grating spectrophotometer between potassium bromide plates. Solution spectra in spectroquality acetonitrile or dichloromethane (Matheson, Coleman and Bell) were obtained using 1.00 mm. cells with calcium fluoride windows.

Results

The electronic spectrum of $Ni(diars)_2Br_2$ in the visible region is representative of this class of compounds and is pictured in Figure 7. At room temperature, the visible region of the spectrum exhibits one broad, slightly asymmetric absorption centered at 21,050 $cm.^{-1}$. At 77°K, there is an increase in ϵ and a narrowing of the central band, and one lower intensity absorption is resolved on either side of the main band. The charge-transfer region of the spectrum of $Ni(diars)_2I_2$ is shown in Figure 8. There is a considerable improvement in resolution of this region of the spectrum at 77°K. Complete results of the spectral study, along with band assignments, are reported in Table II.

$Ni(diars)_2(ClO_4)_2$. Conductivity, infrared, and visible spectral

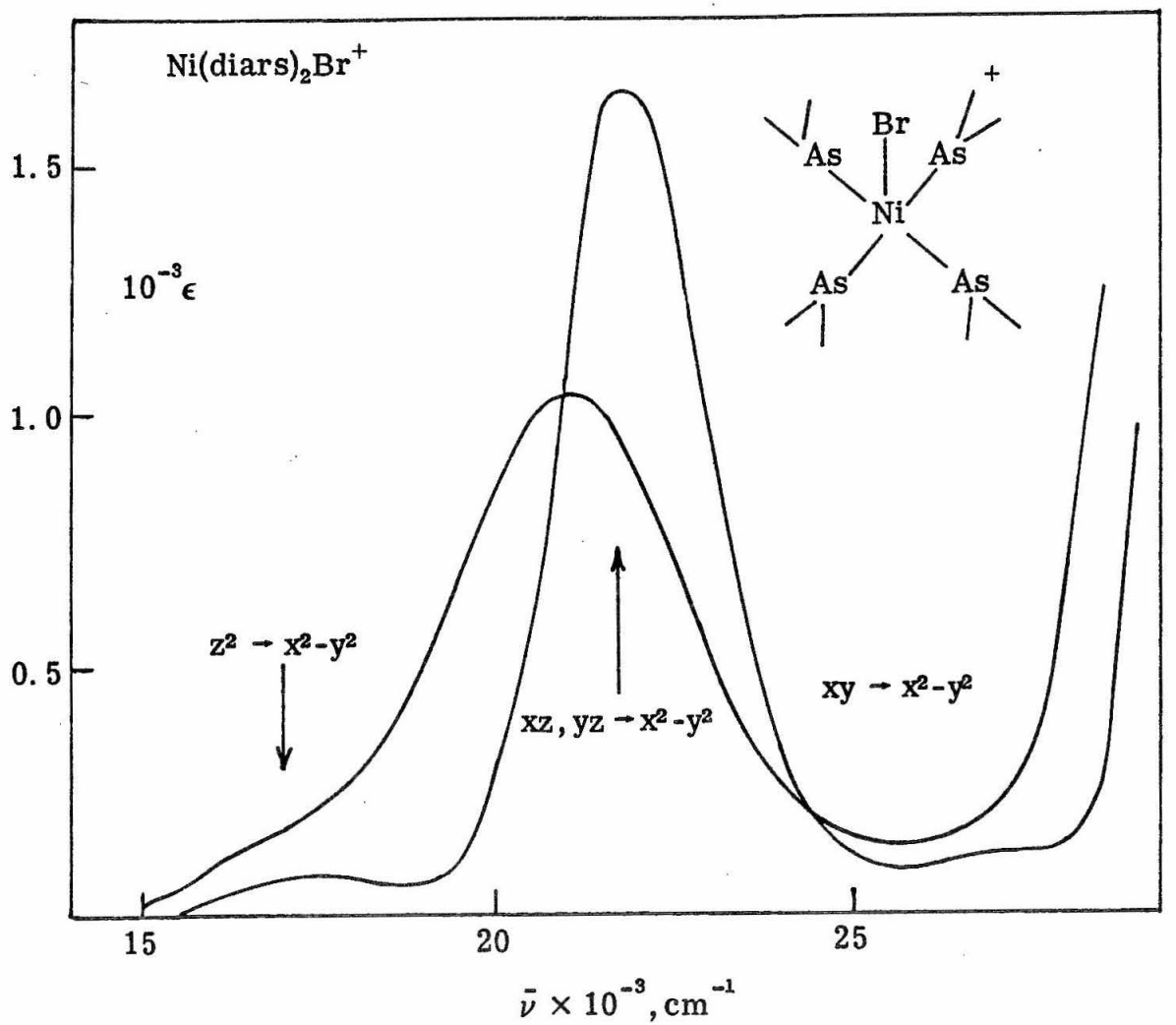

Ni(diars)$_2$Br$^+$
1.5
1.0
0.5
$10^{-3}\epsilon$
Br
As
As
Ni
As
As
+
$z^2 \rightarrow x^2-y^2$
$xz, yz \rightarrow x^2-y^2$
$xy \rightarrow x^2-y^2$
15
20
25
$\bar{\nu} \times 10^{-3}, cm^{-1}$

Figure 7

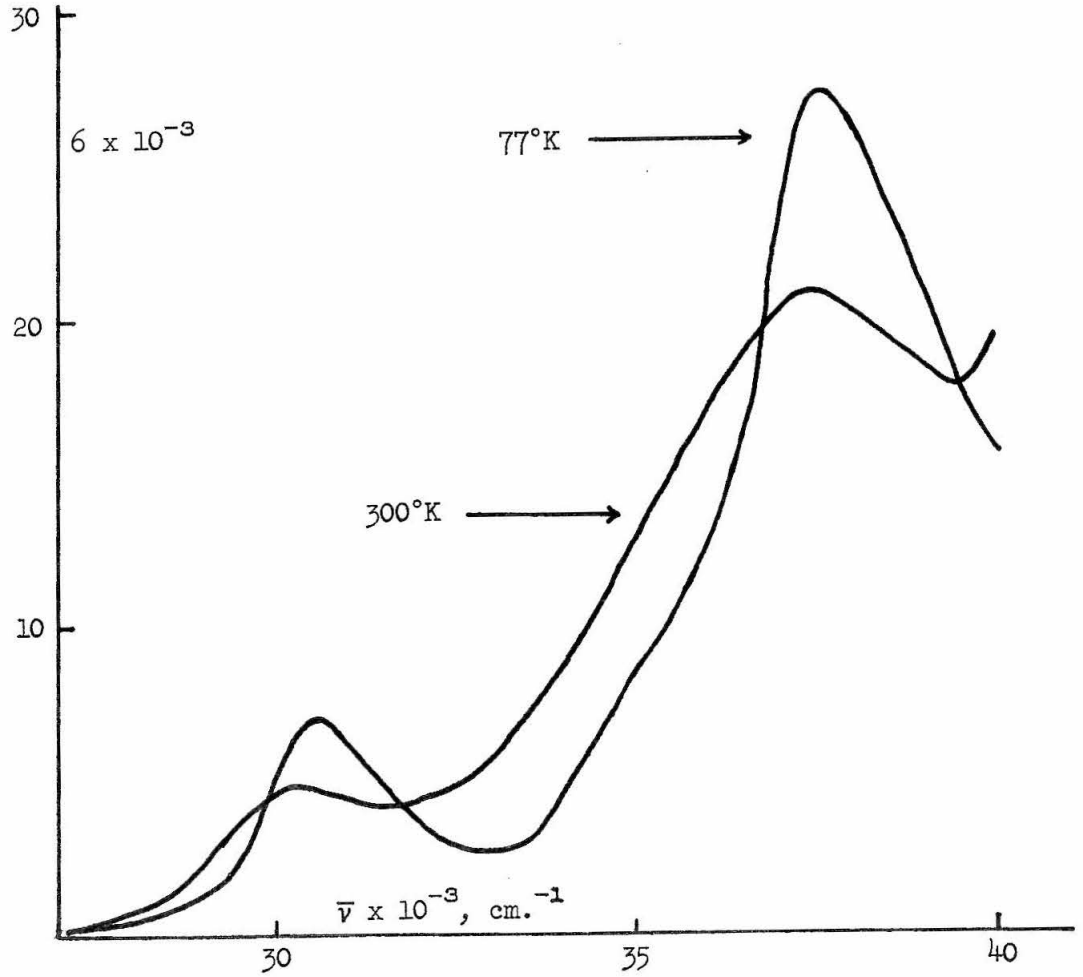


Figure 8. Electronic Spectrum of $Ni(diars)_2I_2$ in 2-methyltetrahydrofuran/methanol (uv region).

Table II

Electronic Spectra of $[Ni(diars)_2X]^{z}$ [a]

	$[Ni(diars)_2CN]ClO_4$		$Ni(diars)(triars)(ClO_4)_2$	
	300°K	77°K	300°K	77°K
$z^2 \rightarrow x^2 - y^2$	18,595 (420)	19,170 (400)	18,555 (765)	18,620 (1150)
$xz,yz \rightarrow x^2 - y^2$	25,945 (1235)	26,415 (1730)	23,040 (1490)	23,365 (2380)
$xy \rightarrow x^2 - y^2$	—	—	—	26,850 (Sh 385)
$As(\sigma) \rightarrow x^2 - y^2$ $(^1A_1 \rightarrow {}^1B_1)$	—	32,205 (Sh 1880)	—	30,650 (Sh 1150)
	—	—	34,525 (7680)	—
$As(\sigma) \rightarrow x^2 - y^2$ $(^1A_1 \rightarrow {}^1E)$	—	—	37,810 (11,400)	37,960 (14,700)
$z^2 \rightarrow \pi^*(CN^-)$	35,300 (11,500)	36,195 (18,400)		
	36,765 (11,700)	37,040 (17,700)		
	$[Ni(diars)_2CNS]ClO_4$		$[Ni(diars)_2(tu)](ClO_4)_2$ [b]	
$z^2 \rightarrow x^2 - y^2$	16,235 (Sh 140)	17,635 (Sh 325)	—	16,425 (.04)[c]
$xz,yz \rightarrow x^2 - y^2$	20,950 (865)	21,600 (1410)	19,740 (1220)	20,940 (.38)[c]
$xy \rightarrow x^2 - y^2$	—	26,665 (Sh 210)	—	—
$X(\pi) \rightarrow x^2 - y^2$	30,355 (2320)	30,580 (3810)	—	29,330 (1.48)[c]
$As(\sigma) \rightarrow x^2 - y^2$ $(^1A_1 \rightarrow {}^1A_1)$	—	—	thiourea absorption	
$As(\sigma) \rightarrow x^2 - y^2$ $(^1A_1 \rightarrow {}^1E)$	37,445 (16,100)	37,970 (21,800)		

Table II--Continued

	$[Ni(diars)_2NO_2]ClO_4$[d]	
	300°K	77°K
$z^2 \rightarrow x^2 - y^2$	16,200 (Sh 135)	16,490 (140)
$xz,yz \rightarrow x^2 - y^2$	21,865 (625)	22,950 (1040)
$xy \rightarrow x^2 - y^2$	—	—
	NO_2^- absorption	

[a] $\bar{\nu}$ $cm.^{-1}$ ($\epsilon,\ell.mole^{-1}cm.^{-1}$). Solvent 2:1 mixture of 2-methyltetrahydrofuran and methanol or ethanol.

[b] Excess thiourea added.

[c] Relative extinction coefficient.

[d] $Ni(diars)_2(ClO_4)_2$ + $NaNO_2$ in solution. Solid compound not isolated.

measurements (99) indicate that this compound exists in solution as the four-coordinate $Ni(diars)_2^{2+}$. The visible spectrum differs from that of the five-coordinate species in two important respects. First, the main ligand field band in the spectrum of this compound is also the lowest energy band. In the five-coordinate species, a less intense band is resolved at lower energy than the main band. Also, the most intense band in the ligand field spectrum of $Ni(diars)_2^{2+}$ appears at higher energy and is of lower intensity than the main band in the five-coordinate complexes. The extinction coefficient of this band shows a marked solvent dependence (see Table III). At room temperature, the visible spectrum of $Ni(diars)_2(ClO_4)_2$ in a 4:1:1 solvent mixture of 2-methyltetrahydrofuran, propionitrile, and ethanol, exhibits one broad band centered at 22,600 $cm.^{-1}$. For a square planar complex involving ligands which are not π-donors, one expects relatively small spacings between the ligand field bands. This point is illustrated by the visible absorption spectra of $Ni(CN)_4^{2-}$, $Pd(CN)_4^{2-}$, and $Pd(NH_3)_4^{2+}$ (26). Also on the basis of a comparison with the separation between the ligand field bands in the spectrum of the five-coordinate species, we tentatively assign the one, broad band in the room temperature spectrum of $Ni(diars)_2^{2+}$ to the three ligand field transitions, $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1B_{1g}$, and ^1Eg $(xy;z^2;xz,yz \rightarrow x^2 - y^2)$.

At 77°K, a weak shoulder is resolved on the high-energy side of this band. It is not possible to give a complete and definitive assignment of these two bands on the basis of our results. A partial assignment is possible, however. Spectral results on the five-coordinate species indicate that, while the true symmetry of the molecule is C_{2v},

Table III

Electronic Spectrum of $Ni(diars)_2(ClO_4)_2$ in Various Solvents

C_2H_5CN	50% C_2H_5OH 50% CH_3CN	98% C_2H_5OH 2% CH_3CN	98% CH_2Cl_2 2% CH_3CN	DMF
22,600 (1140)	22,675 (840)	22,725 (715)	22,600 (330)	a
—	—	30,830 (Sh 2300)	30,040 (4500)	—
34,600 (Sh 15,800)	34,405 (Sh 15,000)	33,615 (Sh 10,400)	33,005 (Sh 11,200)	(35,100)
—	—	—	35,555 (Sh 18,000)	—
38,550 (25,600)	38,460 (25,200)	a	38,740 (25,600)	37,505

[a]Not measured.

the electronic spectra of those complexes can be satisfactorily interpreted by assuming the point microsymmetry C_{4v}. For $Ni(diars)_2^{2+}$, then, we assume the point microsymmetry D_{4h}. None of the three spin-allowed ligand field transitions is symmetry-allowed under D_{4h}. The $^1A_{1g} \rightarrow {}^1Eg$ ($xz,yz \rightarrow x^2 - y^2$) transition is parity-forbidden, and is the only one of the ligand field bands which would become symmetry-allowed if unequal solvent interactions above and below the $Ni(diars)_2^{2+}$ plane removed the center of symmetry possessed by the isolated four-coordinate species. In view of the known tendency of this unit to increase its coordination number to five, it is expected that in coordinating solvents there should be a partial relaxation of the $g \not\rightarrow g$ selection rule because of slightly unequal interactions on either side of the $Ni(diars)_2^{2+}$ plane. Perhaps the best evidence for such interactions is the solvent dependence of the extinction coefficient (ϵ) of the main ligand field band at room temperature. The value of ϵ for this band is significantly greater in the strong donor solvent, acetonitrile, than it is in ethanol (see Table III). By analogy with the five-coordinate case, in which the most intense ligand field band is assigned as the symmetry-allowed $^1A_1 \rightarrow {}^1E$ ($xz,yz \rightarrow x^2 - y^2$) transition, we assign the solvent dependent ligand field band in the spectrum of $Ni(diars)_2^{2+}$ as $^1A_{1g} \rightarrow {}^1Eg$ ($xz,yz \rightarrow x^2 - y^2$).

The shoulder which is resolved on the high energy side of this band at 77°K falls at essentially the same position and has about the same ϵ as the band which has been assigned as $^1A_1 \rightarrow {}^1A_2$ ($xy \rightarrow x^2 - y^2$) in the five-coordinate complexes. It is tempting to assign this band as $^1A_{1g} \rightarrow {}^1A_{2g}$ ($xy \rightarrow x^2 - y^2$) for this reason, since removal of X is not

expected to have much effect on the relative energies of these two orbitals. Such an assignment would place xy < xz, yz in energy. No more spectral bands are resolved in the ligand field spectrum, and it remains to place the dz^2 level. On the basis of the observed spectrum, it appears that the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($z^2 \rightarrow x^2 - y^2$) band could be buried beneath the intense ligand field band, $^1A_{1g} \rightarrow {}^1Eg$, or beneath the charge-transfer bands, with $\tilde{\nu} \gtrsim 29{,}000$ cm.$^{-1}$. On the basis of the variation in position of the $^1A_1 \rightarrow {}^1B_1$ band in the various five-coordinate species (2750 cm.$^{-1}$) and the difference in position between the $^1A_1 \rightarrow {}^1E$ band in the five-coordinate case and that in the four-coordinate case (3200 cm.$^{-1}$), it seems unlikely that the $^1A_1 \rightarrow {}^1B_1$ band in the five-coordinate species should shift by $\gtrsim 10{,}000$ cm.$^{-1}$ upon removal of the fifth ligand. Neglecting the effects of interelectronic repulsion, we then tentatively propose the d-level ordering xy < xz, yz ~ $z^2 \ll x^2 - y^2$ for the four-coordinate $Ni(diars)_2^{2+}$.

The uv absorption spectrum of diarsine alone shows a relatively featureless, rising absorption that begins at ~ 35,000 cm.$^{-1}$. The absorption spectra of the complexes can be measured out to ~ 40,000 cm.$^{-1}$, applying a relatively small baseline correction for the absorbance due to diarsine. As may be noted in Table III, the uv spectrum of $Ni(diars)_2^{2+}$ exhibits a shoulder at ~ 30,000 cm.$^{-1}$ in some solvents and not in others. A shoulder is present near 30,000 cm.$^{-1}$ in the room temperature spectrum in ethanol, methanol, and dichloromethane, and absent in acetonitrile, propionitrile, and dimethylformamide. A resolved band appears at approximately this position in the room temperature spectra of the five-coordinate species for which X is a π-donor (I,Cl,Br,CNS,tu), but is absent in

$Ni(diars)(triars)^{2+}$ which has the σ-donor As in the fifth position. This band has been assigned $X(\pi) \rightarrow M(d\sigma^*)$ in those five-coordinate species. For this reason, it may be speculated that in the spectrum of $Ni(diars)_2^{2+}$, the presence of this band should be due to the charge-transfer transition $Solvent(\pi) \rightarrow M(d\sigma^*)$. Comparing the π-donor ability of the solvents studied with the presence or absence of this shoulder indicates that this assignment may be justified. It is also quite possible that the band is present in the spectra in acetonitrile and DMF, but simply not resolved due to broadening. For these species, uv spectral bands are broader in DMF and acetonitrile. Unfortunately, it has only been possible to measure the low temperature spectrum in the solvent mixture already mentioned. The room temperature spectrum in this solvent does exhibit the shoulder. Obviously it is desirable to measure the low temperature spectrum in a solvent which does not exhibit the shoulder at room temperature, on the chance that it might be resolved at 77°K. The proper solvent system for this measurement has not been found to date. Another possible assignment for the band is as a forbidden component of the $As(\sigma) \rightarrow M(d\sigma^*)$ charge-transfer transition. The assignment of this band will be discussed further in connection with the five-coordinate spectra.

The higher energy region of the uv spectrum is quite similar to that observed in the five-coordinate species studied here, both the square pyramids and the trigonal bipyramids previously discussed. There is one intense absorption maximum at ~ 38,000 $cm.^{-1}$, and one (in one case, two) shoulder(s) on the low energy side of the band. There are three possible $As(\sigma) \rightarrow M(d\sigma^*)$ charge-transfer transitions, $^1A_{1g} \rightarrow {}^1E_u$,

$^1A_{1g}$, and $^1B_{1g}$. Of these, only the former is fully allowed, and so the absorption maximum at 38,000 cm.$^{-1}$ is assigned as this transition. The oscillator strength (f) of this band is independent of temperature, indicating the dipole-allowed nature of the band. The shoulders on the low-energy side of this band are assigned to the other, orbitally-forbidden components of the As(σ) → M($d\sigma^*$) transition. Because diarsine itself begins to absorb ~ 35,000 cm.$^{-1}$, it is conceivable that one or more of the shoulders may be simply due to internal ligand bands, possibly slightly perturbed by the presence of the metal ion. This cannot be ruled out, but is regarded as unlikely, because the absorption due to the complex is generally at lower energy (33,000-35,000 cm.$^{-1}$) than is the diarsine absorption, and the shoulders which appear are considerably better resolved and of higher intensity than in the diarsine spectrum.

Ni(diars)(triars)$(ClO_4)_2$. X-ray structural work by P. J. Pauling has shown this compound to be five-coordinate, with a regular square pyramidal structure (109). The nickel atom is raised slightly above the plane of the four arsenic atoms. The visible absorption spectrum of the solid in Nujol mull is found to be the same as the solution spectrum, both at room temperature and 77°K. At room temperature, the visible spectrum exhibits two bands, at 18,555 cm.$^{-1}$ and 23,040 cm.$^{-1}$, with extinction coefficients of 765 and 1490, respectively. The bands narrow at low temperature and the extinction coefficients increase, to 1150 and 2380, but the positions are relatively unchanged. On the high-energy side of these a less intense (ϵ=380) shoulder is resolved at low temperature. Comparing the visible region of the spectrum of the compound with that of $Ni(diars)_2^{2+}$, the main difference is the band (ν_1) which appears

at 18,555 cm.$^{-1}$ in this case, and is absent in the four-coordinate species. Also, the main ligand field absorption (~ 23,000 cm.$^{-1}$) is considerably more intense for the five-coordinate Ni(diars)(triars)$^{2+}$. On the basis of a simple ligand field picture, we assign the new band at 18,555 cm.$^{-1}$ as the $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$) electronic transition. The most intense band (ν_2) is again assigned as $^1A_1 \rightarrow {}^1E$ ($xz,yz \rightarrow x^2 - y^2$), which is symmetry-allowed under C_{4v}. In accord with this assignment is the observation that the oscillator strength (f) of ν_2 is independent of temperature while that of ν_1 decreases upon lowering the temperature. The weaker shoulder at ~ 27,000 cm.$^{-1}$ is assigned as $^1A_1 \rightarrow {}^1A_2$ ($xy \rightarrow x^2 - y^2$). This transition should involve a smaller dipole change than the others, and is expected to be less intense. The rather high intensity exhibited by all the ligand field bands reflects the fact that the so-called "ligand-field levels" must have a significant amount of arsenic character. Ligand field bands with high extinction coefficients are known to be characteristic of complexes involving ligands with heavy donor atoms (P,As,S,Se) (8,17). This is generally attributed to the inclusion of considerable ligand character in the MO's derived from the metal d-orbitals in these complexes. The highest value of ϵ which has been reported for a ligand field band involving a first-row transition metal ion is 9800, for the first ligand field band in the trigonal bipyramidal complex, [Ni(QAS)NCS]ClO_4 (133).

The charge-transfer spectrum of Ni(diars)(triars)$^{2+}$ exhibits an intense band at 37,000 cm.$^{-1}$, which is assigned to the allowed $^1A_1 \rightarrow {}^1E$ component of the As(σ) $\rightarrow$ d(σ^*) transition. There is also a quite weak shoulder revealed in the low temperature spectrum at ~ 30,700 cm.$^{-1}$.

Since the As atom does not possess π-donor orbitals, the only reasonable assignment is to some orbitally-forbidden As(σ) → d(σ*) transition. There is a decrease in intensity of this band at low temperature, indicating the vibronically-allowed nature of the band (122). The observed extinction coefficient ($\epsilon \sim 1000$) is appropriate for a symmetry-forbidden charge-transfer band.

[Ni(diars)$_2$X$^+$];(X=Cl,Br,I). In order to verify the five-coordinate composition of these compounds in solution, we have measured the absorption spectra of both Ni(diars)$_2$X$_2$ and [Ni(diars)$_2$X]ClO$_4$. The results are given in Table IV, and it is quite apparent that the spectra of Ni(diars)$_2$X$_2$ and [Ni(diars)$_2$X]ClO$_4$ are the same for any particular X, and are readily distinguished from that of Ni(diars)$_2^{2+}$. Since we can tell that no four-coordinate species is present, all the complex must be in the five-coordinate form, because [Ni(diars)$_2$X]ClO$_4$ could give a six-coordinate Ni(diars)$_2$X$_2^0$ species only in the presence of a corresponding amount of Ni(diars)$_2^{2+}$, by reason of the stoichiometry. Dissociation of [Ni(diars)$_2$X]^Z to Ni(diars)$_2^{2+}$ + X^{Z-2} in the concentration range employed for the spectral measurements appears to occur only with X = thiourea, and this dissociation is easily detected by observing a very asymmetric main ligand field band in the visible region of the spectrum at 77°K. One component of this composite peak falls at approximately the position of the main absorption in Ni(diars)$_2^{2+}$ ($\tilde{\nu} \simeq 23{,}000$ cm.$^{-1}$), the other at lower energy.

The pattern of three bands in the visible region which was observed in the spectrum of Ni(diars)(triars)$^{2+}$ at 77°K appears in this case also. The assignment of the visible spectrum of Ni(diars)$_2$X$^+$ is the

Table IV

Comparison of Electronic Spectra of $Ni(diars)_2X_2$ and $[Ni(diars)_2X]ClO_4$ [a]

	$Ni(diars)_2Cl_2$		$[Ni(diars)_2Cl]ClO_4$	
	300°K	77°K	300°K	77°K
$z^2 \rightarrow x^2 - y^2$	—	18,030 (Sh 65)	—	—
$xz,yz \rightarrow x^2 - y^2$	21,285 (1060)	22,080 (1530)	21,270 (905)	22,065 (1270)
$xy \rightarrow x^2 - y^2$	25,895 (Sh 170)	26,285 (190)	—	26,345 (290)
$X(\pi) \rightarrow x^2 - y^2$	30,345 (Sh 3740)	30,425 (4670)	30,245 (Sh 2360)	30,455 (3420)
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_1 \rightarrow {}^1A_1$)	33,410 (Sh 9340)	34,275 (Sh 11,220)	33,265 (Sh 9050)	34,275 (Sh 9340)
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_1 \rightarrow {}^1E$)	36,245 (Sh 21,500)	36,695 (37,800)	36,285 (Sh 19,000)	36,940 (30,400)
	40,000 (Sh 21,000)	40,715 (20,000)	39,960 (Sh 17,700)	40,700 (15,300)
	$Ni(diars)_2Br_2$		$[Ni(diars)_2Br]ClO_4$	
$z^2 \rightarrow x^2 - y^2$	16,395 (Sh 110)	17,660 (80)	16,325 (Sh 154)	17,560 (165)
$xz,yz \rightarrow x^2 - y^2$	21,055 (1030)	21,820 (1820)	21,055 (1025)	21,860 (1960)
$xy \rightarrow x^2 - y^2$	—	26,275 (Sh 110)	—	27,025 (Sh 260)
$X(\pi) \rightarrow x^2 - y^2$	30,625 (Sh 5300)	30,675 (Sh 5180)	30,660 (Sh 5950)	30,315 (Sh 5600)
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_1 \rightarrow {}^1A_1$)	—	33,280 (Sh 6950)	—	33,110 (Sh 6470)
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_1 \rightarrow {}^1E$)	38,240 (24,000)	38,095 (33,800)	37,901 (26,000)	37,996 (33,800)

Table IV--Continued

	$Ni(diars)_2I_2$		$[Ni(diars)_2I]ClO_4$	
	300°K	77°K	300°K	77°K
$z^2 \rightarrow x^2 - y^2$	16,130 (Sh 170)	17,330 (165)	16,230 (Sh 330)	17,305 (190)
$xz,yz \rightarrow x^2 - y^2$	20,265 (1145)	21,455 (1950)	20,275 (1075)	21,465 (1850)
$xy \rightarrow x^2 - y^2$	—	26,665 (Sh 225)	—	27,025 (Sh 230)
$X(\pi) \rightarrow x^2 - y^2$	30,035 (Sh 5250)	30,245 (7500)	30,155 (Sh 4900)	30,245 (6450)
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_1 \rightarrow {}^1A_1$)	—	34,365 (Sh 7000)	—	34,070 (Sh 5800)
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_1 \rightarrow {}^1E$)	37,075 (22,750)	37,620 (30,500)	37,200 (20,800)	37,265 (27,300)
	$Ni(diars)_2(ClO_4)_2$			
$xz,yz \rightarrow x^2 - y^2$ ($z^2 \rightarrow x^2 - y^2$)	22,600 (440)	23,200 (880)		
$xy \rightarrow x^2 - y^2$	—	26,250 (Sh 195)		
$Solvent(\pi) \rightarrow x^2 - y^2$ or $As(\sigma) \rightarrow x^2 - y^2$ ($^1A_{1g} \rightarrow {}^1A_{2g}$)	30,870 (Sh 2880)	31,665 (Sh 1580)		
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_{1g} \rightarrow {}^1A_{1g}$)	33,650 (Sh 1.82)			
$As(\sigma) \rightarrow x^2 - y^2$ ($^1A_{1g} \rightarrow {}^1E_u$)	37,365 (28,500)	38,735 (27,200)		
		{35,590 / 36,495} (17,800)		

[a] $\bar{\nu}$ cm.$^{-1}$ (ϵ,ℓ.mole^{-1}cm.$^{-1}$). Solvent 2-methyltetrahydrofuran-methanol or ethanol; ethyl ether-ethanol. Some ϵ's determined in methanol. Solvent for $Ni(diars)_2(ClO_4)_2$ is 4:1:1 2-methyltetrahydrofuran-ethanol-propionitrile.

same as that proposed for Ni(diars)(triars)$^{2+}$. One difference in the spectra is that for Ni(diars)$_2$X$^+$, the central band (ν_2) clearly dominates the spectrum, and considerably weaker bands appear on either side of the main peak. This pattern is expected in C_{4v}, since one ligand-field band is symmetry-allowed and the other two are symmetry-forbidden. The reason for the relatively high intensity of ν_1 for Ni(diars)(triars)$^{2+}$ is most likely that the $a_1(z^2)$ orbital has a significant amount of ligand character in that case. Mixing of ligand orbitals with metal d-orbitals is expected to be considerably stronger for arsenic than for halide. In accord with this interpretation is the observed dependence of ϵ for ν_1 on X in the halide series. ϵ decreases in the order I > Br > Cl, which is also the order of decreasing tendency to form covalent bonds with metal ions. This is evidence in favor of the assignment of ν_1 as $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$), because the dz^2 orbital interacts most strongly with orbitals on As, Cl, Br, and I.

The usefulness of the low temperature ligand field spectrum is best seen for these halide complexes, where the room temperature spectrum shows one broad band with a shoulder on one side or the other of this main band. All three bands can be detected in each of the spectra at 77°K (see Table IV). The oscillator strength of ν_2 is not changed on decreasing the temperature, which is strong evidence of the symmetry-allowed character of the band (122). Because the weaker bands appear as shoulders, it is not possible to measure the half-widths or to obtain accurate values of ϵ. It does appear, however, that the lowest energy band decreases in intensity at low temperature.

The band assigned as $^1A_1 \rightarrow {}^1B_2$ ($xy \rightarrow x^2 - y^2$) is relatively

weak, and appears in the same position for these complexes as was reported for $Ni(diars)_2^{2+}$ and $Ni(diars)(triars)^{2+}$. The position of the other two ligand field bands does change, the energy ordering being Cl > Br > I for both bands. A rationalization for this ordering will be offered later. There is also a striking shift of these two bands to higher energy at low temperature, in some cases by more than 1000 $cm.^{-1}$. This could reflect a small change in the position of the fifth ligand at low temperature, or the freezing out of the X-exchange process which is known to occur at room temperature (see Appendix I). For that matter, it is known that the whole metal-arsenic framework is rather flexible. There may be a detectable change in the equilibrium positions of the metal and ligand atoms with temperature.

The charge-transfer spectrum of $Ni(diars)_2X^+$ (X=Cl,Br,I) exhibits the strong absorption at ~ 37,000 $cm.^{-1}$ which is characteristic of the complexes under study, and is assigned as before. A shoulder on the low-energy side of this main band appears at low temperature, and is assigned as the $^1A_1 \rightarrow {}^1A_1$ (allowed) component of the $As(\sigma) \rightarrow d(\sigma^*)$ transition. The exact position of this band is difficult to locate because it appears as a shoulder in every case. It does appear that as with the main $As(\sigma) \rightarrow d(\sigma^*)$ band, the position is not constant, but shows small variations with X in an unpredictable fashion.

In each of the halides, a pronounced shoulder appears in the room temperature spectrum at ~ 30,000 $cm.^{-1}$. This band is resolved at 77°K, but the position of the band is relatively unchanged in the series Cl, Br, I. In all six compounds measured, the bands fall within a range of 500 $cm.^{-1}$. The striking constancy in the position of this band led

Meek to assign it as a phosphine-to-metal charge-transfer band in his five-coordinate SPY complexes (106,108,134). In $Ni(VPP)X^+$, he observed a spread of 670 $cm.^{-1}$ for this band in the chloride, bromide, iodide, and thiocyanate, with an average position of 29,120 $cm.^{-1}$ (106). This is the band which appears in the spectrum of $Ni(diars)_2^{2+}$ in certain solvents and is not observed (at room temperature) in others. The room temperature spectrum of $Ni(diars)(triars)^{2+}$ is featureless here at room temperature, but at 77°K, a rather weak shoulder appears. The extinction coefficient of this shoulder is ~ 1000, while for X = Cl, Br, I ϵ for the maximum is 3750-5500. The observed extinction coefficient for this band is quite sensitive to the nature of X, increasing in the order Cl < Br < I. This was also observed by Meek, who reports for the band at ~ 29,120 $cm.^{-1}$ in the $Ni(VPP)_2X^+$ complexes extinction coefficients of 12,220, 13,230, and 25,930 for the chloride, bromide, and iodide, in dichloromethane solution. This is evidence in favor of the assignment of this band as $X(\pi) \rightarrow M(d\sigma^*)$.

In the trigonal-bipyramidal compounds studied, we observed a band in this region (26,500-32,000 $cm.^{-1}$) which showed a variation in position in the order Cl > Br > I. This band was assigned as $X(\pi) \rightarrow M(d\sigma^*)$. In the TBP complexes of the type $Ni(TAP)X^+$, the position of the $X(\pi) \rightarrow M(d\sigma^*)$ transition covers a range of 4390 $cm.^{-1}$ (X=Cl,Br,I). The analogous band in the spectrum of $Ni(TMP)_3Br_2$ was also assigned in this way. While it is disturbing that this band in the SPY's does not vary in the predicted fashion for a halide(π) → metal($d\sigma^*$) charge-transfer band, all other evidence points toward this assignment. There is no other band in the observed spectrum which can be logically assigned to

this transition, and the evidence from the trigonal-bipyramidal cases is that this transition should occur well below 40,000 $cm.^{-1}$. We assign the band at 30,000 $cm.^{-1}$ to the allowed charge-transfer transition $^1A_1 \rightarrow {}^1E$ $(X(\pi) \rightarrow x^2 - y^2)$.

It is rather unlikely that the energy of the MO derived from the metal $dx^2 - y^2$ orbital should vary much in the halides. An alternative explanation for the invariance in position of this charge-transfer band is the somewhat unconventional suggestion that the energies of the MO's derived mainly from the halide π-donor levels do not vary drastically from chloride to bromide to iodide. This is perhaps conceivable if the iodide level is more strongly stabilized by interaction with the metal d-orbital than is the chloride. Stephenson has determined the crystal and molecular structure of the six-coordinate bis-diarsine platinum(II) complexes with chloride and iodide, and reports a much longer Pt-X bond distance for the chloride than for the iodide. (Pt-Cl, 4.16 Å; Pt-I, 3.50 Å) (19,20). He interprets these distances as indicating an essentially electrostatic bond in the chloride and a covalent bond in the iodide. While it is true that the six-coordinate, solid platinum complex is not the five-coordinate nickel complex in solution, it seems likely that this trend will be the same in the two cases. A longer Ni-X distance for the chloride than for the iodide would considerably reduce the metal-chloride(π) interaction, in comparison to the iodide(π) interaction. If the Ni-X distance in the five-coordinate complex in solution varies in the order Cl > Br > I, then the degree to which the $X(\pi)$ level is depressed should vary in the order I > Br > Cl. But in the free atoms, the relative positions of the $X(\pi)$ levels are

I > Br > Cl. So by this mechanism, the position of the X(π) levels in the complex may be brought closer together. It is also possible that electronic repulsion effects may operate as well to cause the absorption bands to occur at closely similar energies. A qualitative argument based on the effect of electron repulsion indicates that this effect should operate to lower the energy of the band in the chloride most, the bromide next, and the iodide least.

It should be noted that in the SPY complexes, the fifth ligand must be placed in the region of a filled dz^2 orbital, which will tend to repel the anionic or neutral ligand X. Unless X is particularly prone to covalent bonding, the result of this repulsion will be to increase the M-X distance as has been observed, and in turn significantly decrease the amount of M-X covalent bonding. In the case of the TBP, the fifth ligand is placed in the region of an empty M(dz^2) orbital. Thus the M-X distance will be normal (114) and the extent of covalent bonding will again be reasonable, in the absence of the filled, repelling orbital. This may explain the difference in behavior observed for the band assigned as X(π) $\rightarrow$ M($d\sigma^*$) in the two cases.

<u>[Ni(diars)$_2$X]^z(X=CN,NO$_2$,CNS,tu).</u> The visible spectra of these compounds are similar to those described above. It is easy to identify the symmetry-allowed $^1A_1 \rightarrow {}^1E$ ($xz,yz \rightarrow x^2 - y^2$) ligand field band ($\nu_2$) by the dependence of the extinction coefficient on temperature. ϵ for this band shows a considerably greater increase than for any other band in the visible spectrum. The value of f for ν_2 is seen to be temperature-independent. The band which appears as a weak shoulder (ν_3) $\sim$ 26,000 cm.$^{-1}$ in the other compounds is not seen in the NO$_2$ or the thiourea

(tu) derivatives because of absorption due to NO_2 and thiourea. This band is not seen in the cyanide either, because in this case, the ($xz,yz \rightarrow x^2 - y^2$) transition appears at ~ 26,000 $cm.^{-1}$.

Certain experimental difficulties were encountered with the thiourea complex. In order to suppress dissociation of the complex in the ethanol/2-methyltetrahydrofuran solvent mixture, a large excess of thiourea had to be added, which rendered the glass unstable and subject to cracking at low temperature. With an insufficient amount of thiourea to suppress dissociation, a stable glass was formed, and the value of $\tilde{\nu}_{max}$ was obtained by extracting it from the asymmetric peak which contained this band and also that due to $Ni(diars)_2^{2+}$. It was confirmed that the composite band was composed of one band due to $Ni(diars)_2^{2+}$ and one due to $Ni(diars)_2tu^{2+}$ by adding a small amount of thiourea and observing the change in the intensities of the two components of the band at 77°K. It is not certain whether the thiocyanate complex contains N- or S-bonded thiocyanate at 77°K in this solvent (see Appendix II). The main ligand field band (ν_2) appears to be symmetric at 77°K, and so does not provide evidence in favor of the coexistence of the two isomers under these conditions. The position of ν_2 should not differ greatly for the two forms, however.

In the uv region, we observe the band at ~ 30,000 $cm.^{-1}$ which has been assigned as $X(\pi) \rightarrow M(d\sigma^*)$, in the thiourea and the thiocyanate, at room temperature and 77°K. Both of these ligands are known to be good π-donors. This region is completely obscured by ligand absorption in the NO_2 derivative. In the cyanide, no absorption band is observed in this region at room temperature. At 77°K, a shoulder appears at

$\sim$ 32,000 cm.$^{-1}$. This may be due to a M $\rightarrow$ CN(π^*) charge-transfer transition, or perhaps to a component of the As(σ) $\rightarrow$ M($d\sigma^*$) band. The allowed $^1A_1 \rightarrow {}^1E$ (As(σ) $\rightarrow$ M($d\sigma^*$)) transition is observed for each of these compounds also at $\sim$ 37,000 cm.$^{-1}$.

Discussion

Related studies. In addition to the ingenious synthetic and characterization studies described earlier, Meek and coworkers have assigned a number of the NiL_2X^+ (square pyramidal complexes) electronic spectra which they have measured (106). This assignment deals with the main ligand field band which appears in the range 18,000-21,000 cm.$^{-1}$, and the lowest energy charge-transfer band, which appears in the range 28,000-30,000 cm.$^{-1}$. They assign the ligand field band as the electronic transition $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$). In no case do they observe more detail in this region of the spectrum than the one, broad ligand field absorption.

Since the position of the band varies in the order Cl > Br > I, they conclude that the band follows the expected spectrochemical series ordering, and is evidence in favor of the assignment. As has been described in some detail, our electronic spectral measurements at 77°K reveal three ligand field bands in the region where a room temperature measurement reveals only one absorption maximum and a weak shoulder. Based on the relative intensities of the bands, and the temperature dependence of the intensity of the main ligand field band (ν_2) we have assigned this band ($\tilde{\nu} \sim$ 21,000 cm.$^{-1}$) as the transition $^1A_1 \rightarrow {}^1E$ ($xz,yz \rightarrow x^2 - y^2$). It is true that the observed variation in position of the ligand field band does obey the traditional octahedral spectrochemical

series ordering. However, the levels being considered here, $a_1(z^2)$ and $b_1(x^2 - y^2)$, do not correspond to the two levels involved in the octahedral or tetrahedral ligand field transitions. In the octahedral case, the unfilled orbital on which the electronic transition terminates is σ-antibonding with respect to the ligand in question. The filled level from which the transition originates interacts with ligand π-type orbitals. In the SPY geometry of the type considered here, the $b_1(x^2 - y^2)$ orbital is essentially non-bonding with respect to X, the fifth ligand, and the $a_1(z^2)$ orbital is σ-antibonding with respect to X. The result of this situation is that the $^1A_1(z^2) \rightarrow {}^1B_1(x^2 - y^2)$ transition should exhibit behavior which is the opposite of that observed in the octahedral case. This is so because in this case the stronger the σ-donor X, the greater will be the destabilization of the $a_1(z^2)$ level, and the lower the energy will be at which the transition should occur. Assigning the band as $^1A_1 \rightarrow {}^1E$ $(xz,yz \rightarrow x^2 - y^2)$ corrects this problem so that the observed ordering of the band position is as expected. Since the π-donor ability ordering is I > Br > Cl, the energy of the e(xz,yz) level should vary in the order I > Br > Cl, and the resulting band ordering should then be Cl > Br > I, as observed.

The other assignment in contention is the first charge-transfer band. In this case the assignment is not clear-cut, as has been pointed out. The reasons set forth to justify our assignment of this band as $X(\pi) \rightarrow M(d\sigma^*)$ in the five-coordinate complexes where X is a π-donor have already been discussed in detail. There are additional results, reported by Meek, which bear on this point.

In the electronic spectra of the four-coordinate $Ni(VPP)X_2$

complexes, the lowest energy charge-transfer band depends on X in the expected fashion for an $X(\pi) \rightarrow M(d\sigma^*)$ charge-transfer band. This band appears at 34,100 $cm.^{-1}$ in the iodide, 36,140 $cm.^{-1}$ in the bromide, 36,230 $cm.^{-1}$ in the thiocyanate, and is not observed below 40,000 $cm.^{-1}$ in the chloride (106). If the correct assignment of the lowest energy charge-transfer band (at 29,000 $cm.^{-1}$) in the $Ni(VPP)_2X^+$ spectrum is $P(\sigma) \rightarrow Md(\sigma^*)$, this same transition would be expected to give rise to the lowest energy charge-transfer band in $Ni(VPP)X_2$ also. That this is not the case is evidence in favor of our assignment of the lowest energy charge-transfer band in NiL_2X^+.

It is not possible to prove the assignment of the lowest-energy charge-transfer band in NiL_2X^+ conclusively without additional experimental evidence. In Proposition I is suggested an experiment using magnetic circular dichroism which could very likely resolve this electronic structural problem. Work is being carried out in our laboratories using liquid crystalline phases to orient molecules in order to study the polarization of spectral bands (135,136). It is clear that determining the band polarizations would resolve the remaining assignment difficulties and serve as a good check for the assignments believed to be correct. Unfortunately, there are not now available suitably polar, nonaqueous liquid crystalline media which will dissolve these compounds. When such media are developed, this problem should be studied using this technique.

Ligand field energies. The assignment of the ligand field bands which has been proposed leads to the d-level ordering $xy < xz, yz < z^2 \ll x^2 - y^2$ for the five-coordinate complexes. This ordering seems reason-

able in terms of a simple ligand field model. By changing only the fifth position and maintaining the $Ni(diars)_2^{2+}$ framework, the main differences in the ligand field spectrum are expected to come as a result of the changing position of the e(xz,yz) level, which matches the X π-orbitals, and the $a_1(z^2)$ level, which matches the X σ-orbital. This is not to say that the $Ni(diars)_2^{2+}$ framework will be unaffected by the fifth ligand; in fact we have found that there is a rather important dependence of the position of the $b_1(x^2 - y^2)$ level on the nature of X. Regardless of the change in the energy of $b_1(x^2 - y^2)$ from one complex to another, it is possible to extract a quantity from the ligand field spectrum which should show the same dependence on X as the traditional ligand field splitting parameter Δ_o. This is done by simply taking the difference in energy of the two lowest energy bands, ν_1 and ν_2. This procedure gives the separation between the $a_1(z^2)$ and e(xz,yz) levels in the complex, neglecting interelectronic repulsion. The values of this parameter are listed in Table V, and lead to the spectrochemical series $CN > NO_2 > As > tu > Br \gtrsim I \gtrsim Cl \gtrsim CNS$. There is very little difference between Br, I, Cl, CNS (277 $cm.^{-1}$), and since this is close to the limits of experimental error, it is unlikely that the ordering from those X has much meaning. It is encouraging that otherwise this constructed spectrochemical series is in agreement with experience with ligand field spectra in the octahedral case (137). The position of CNS in this constructed series may indicate that under these conditions it is S-bonded.

It was recognized during the course of this work that the system chosen for study might be capable of providing useful information of a type heretofore unavailable, concerning bonding properties of ligands.

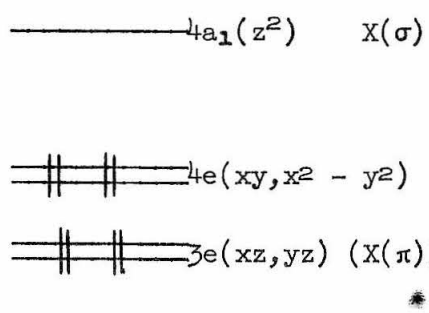
Table V

Spectrochemical Series Parameter Δ' from Electronic Spectra of Square Pyramidal Complexes

Compound	Δ' $(=\nu_2 - \nu_1)$
$Ni(diars)_2CN^+$	7246 $cm.^{-1}$
$Ni(diars)_2NO_2^+$	6461
$Ni(diars)(triars)^{2+}$	4745
$Ni(diars)_2(tu)^{2+}$	4512
$Ni(diars)_2Br^+$	4229
$Ni(diars)_2I^+$	4142
$Ni(diars)_2Cl^+$	4053
$Ni(diars)_2CNS^+$	3961

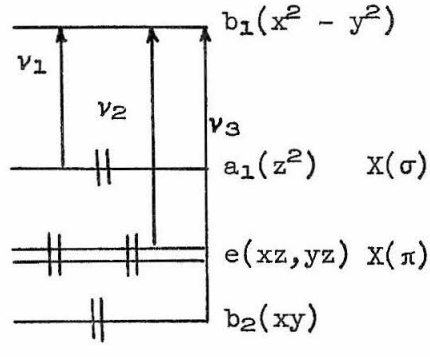
The basic problem which arises in studying the bonding properties of ligands by measuring ligand field splittings is that in the well-studied cases, σ-bonding effects and π-bonding effects are not directly separable. In the octahedral case, the t_{2g} orbitals interact with ligand π-orbitals and the e_g set interacts with ligand σ-orbitals, so that Δ_o is a measure of the difference between σ-donor ability and π-donor ability. The situation in tetrahedral symmetry is just as inconclusive. In square planar geometry the situation is somewhat different, but still rather difficult, because ligand field bands are not generally well separated. It is apparent that what is needed is a system which contains a basic "building block," capable of readily adding different ligands (X) to be tested, and a geometry in which certain metal d-orbitals interact only with the "building block" ligands and others interact only with X. Attempts to construct a system of this type have been carried out using the low spin cobalt(III) complexes of the type $[Co^{III}(NH_3)_5X]$ (138). Attempts to separate σ- and π-effects using this system were unsuccessful, partly because there was not a complete separation of the effects of X and NH_3 ligands on the metal d-orbitals.

In the TBP complexes discussed in Chapter 2 we have a partial solution to the problem. In that case, the d-level scheme is as pictured below



The 4e orbitals ($xy, x^2 - y^2$) are non-bonding with respect to X. Thus the position of the first ligand field band should reflect the σ-donor ability of X. As has been pointed out, this correlation appears to fit well. The second ligand-field band, however, is a mixed σ-π transition.

The square pyramidal system of the type studied here appears to be a good choice for attempting to distinguish between σ- and π-effects spectroscopically. The d-level ordering in this case is pictured below, and gives rise to three possible transitions, one which should reflect π-donor or acceptor ability (ν_2), and one which should be independent of X and serve as a calibration point (ν_3).



In order for this method to work, it is essential that either $b_1(x^2 - y^2)$ or $b_2(xy)$ remain of constant energy from one complex to another. To a first approximation, these levels should be independent of X. Assuming that the energy of $b_1(x^2 - y^2)$ is independent of X, we expect ν_1 to exhibit the energy ordering CN < NO_2 < As < halide. The observed ordering is NO_2 < As < halide < CN, which is very different. The energy ordering exhibited by ν_2 is CN > As > NO_2 > Cl > Br > CNS > I > tu, which is in better agreement with expectation than is the ordering exhibited by ν_1, but is still not entirely correct. If the assignment of

the ligand field spectrum is correct, the only conclusion which may be drawn is that the energy of the $b_1(x^2 - y^2)$ level must depend upon the nature of X in some unspecified way. The effect of X must be somehow transmitted through the $Ni(diars)_2^{2+}$ framework. That this effect is observed is perhaps not surprising. Introducing X into the region of the occupied $a_1(z^2)$ orbital could very likely alter the electronic distribution about the central metal atom, thus changing the $Ni(diars)_2^{2+}$ geometry slightly.

Even though the energy of the $b_1(x^2 - y^2)$ level is dependent upon X, it might still be possible to obtain σ- and π-donor orderings if the energy of $b_2(xy)$ is independent of X. The $^1A_1 \rightarrow {}^1A_2$ ($xy \rightarrow x^2 - y^2$) transition can be observed for four of the eight X, but is a weak shoulder in two of these cases, and the exact position is difficult to pinpoint. Using the $^1A_1 \rightarrow {}^1A_2$ transition as a reference point, which is equivalent to assuming a constant value for the energy of the b_2 level for these complexes, apparently leads to an unlikely result; that is, I > Br > Cl > As for σ-donor ability. The halide ordering is probably correct, but As is certainly out of place. This result may arise from a change in position of b_2, or simply from the difficulty of locating with any accuracy the $^1A_1 \rightarrow {}^1A_2$ transition in the Ni(diars)(triars)$^{2+}$ spectrum. In any case, it is unfortunate that this transition is not resolved in the cases of X = CN, NO_2, tu, because these are the cases for which ν_1 is badly out of order.

There are two further possibilities which might be considered, concerning the unexpected behavior of ν_1 in these spectra. The first is that perhaps electron-repulsion effects are very large for ν_1 and

hence the values of ν_1 do not correspond at all closely to energy separations. This explanation is regarded as unlikely. One reason for this is simply that chloride and cyanide, for which the values of ν_1 are definitely not as predicted, appear at approximately the same position in the nephelauxetic series (14). This series indicates the extent of metal d-electron delocalization by the ligand, and thus the magnitude of the effect which interelectronic repulsion should have on spectral bands. The other possibility is that the ligand field spectrum may be improperly assigned. As was indicated previously, the assignment of ν_2 is regarded as rather certain. Another assignment of the other ligand-field bands has been considered. This scheme leads to a better, though still not ideal ordering of the band assigned as $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$). However, it does have other rather unappealing features. In this scheme, ν_1 is assigned as the spin-forbidden transition $^1A_1 \rightarrow {}^3E$ ($xz,yz \rightarrow x^2 - y^2$) for X = Cl, Br, I. For X = As, CN, NO_2, ν_1 is assigned as before, $^1A_1 \rightarrow {}^1B_1$. In the halides, ν_3 is assigned as $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$). This results in the energy ordering halide > As > CN > NO_2 for $^1A_1 \rightarrow {}^1B_1$, and the inverse ordering for the position of the $a_1(z^2)$ level. This ordering is still not exactly as predicted, since NO_2 appears to be out of order. It also involves inverting the d-level ordering in the halides to $xy < z^2 < xz, yz \ll x^2 - y^2$, which seems unlikely. Finally, this scheme requires the assignment of a band with ϵ = 200, 80, 70 for X = I, Br, Cl as a spin-forbidden ligand field transition. These intensities appear considerably too high for spin-forbidden bands in a complex of nickel(II) (26). For these reasons, we conclude

that the present assignment is probably the one most consistent with experience.

Comparison with trigonal-bipyramidal spectra. We have a good system here for comparison between the electronic spectral characteristics of the two limiting geometries in five-coordination, the trigonal bipyramid (TBP) and the square pyramid (SPY). It was anticipated that it might be possible to come up with some rough empirical guidelines for classifying five-coordinate complexes as SPY or TBP on the basis of the electronic spectrum measured at room temperature and 77°K. Progress has been made along these lines, using the data presented here and also other work recently completed in our laboratories (124). We consider only the case of the low-spin d^8 complexes, primarily involving nickel(II) as the central metal. There are a reasonable number of complexes of this type for which structural determinations have been carried out, and it would be worthwhile to carry out detailed spectral measurements and apply the guidelines discussed below to some of these compounds which have not been the subject of careful spectral study.

In six compounds used for comparison here the coordinated ligand atoms are identical, the only difference besides the geometry of the two complexes being the nature of the aliphatic and aromatic groups attached to the arsenic donor atoms. These six compounds are $Ni(diars)_2X^+$ (X=Cl, Br,CN) and $Ni(TAA)X^+$ (X=Cl,Br,CN).

The one characteristic of the visible spectrum which is diagnostic of the TBP is the intense, asymmetric room temperature band which becomes more symmetrical at 77°K. This has been discussed in some detail

in Chapter 2. The SPY structures do not exhibit this behavior (compare Figs. 1, 2, and 7). Rather, bands appearing as shoulders in the room temperature spectrum of the SPY complexes are resolved at 77°K. This is perhaps best seen in the spectrum of Ni(diars)(triars)$^{2+}$, in which two bands that appear close together and are of comparable intensity are resolved at 77°K.

The number and intensity pattern of the ligand field bands, as well as their temperature dependence, are useful in diagnosing the geometry. The TBP complexes mentioned above exhibit two bands, the one at lower energy considerably more intense. The less intense band is sometimes difficult to observe because it is often as little as one-fiftieth as intense as the main band. The main band is often asymmetric at 300°K, and there is some evidence, discussed previously, for the generalization that the degree of asymmetry depends upon the static distortion of the TBP complex. For some complexes, though none of the group under discussion here, the asymmetric band gives way to two, distinct bands at 300°K. This is the case for $Ni(TMP)_3X_2$ (TMP=trimethylphosphine,X=Br,I) (124). The lower energy component is of lower intensity in the cases observed thus far. This is consistent with the idea that the spectral pattern in such complexes is changing over to the SPY.

The SPY complexes ($Ni(diars)_2X^+$ exhibit three ligand field bands, the central one the most intense. In every case examined in this study, the SPY structure does show the less intense, lowest energy band at 77°K, and often does at room temperature also. The highest energy one (ν_3) of the three ligand field bands is occasionally not observed. The charge-transfer spectra of the TBP and SPY complexes compared here are

rather similar, and not particularly useful for distinguishing one structure from another. The positions of the ligand-field bands can be useful in distinguishing the two structures. It should be noted that the low-spin limitation which we have imposed will only be met using relatively strong-field ligands. For example, Ciampolini (112), Dori (139), and others (113,140) have prepared a number of high-spin, five-coordinate nickel(II) complexes using nitrogen and oxygen donor ligands. The common type of low-spin d^8, five-coordinate complex involves some cyanide, phosphine, or arsine ligands.

The known mixed halide-phosphine (or arsine) TBP's of nickel(II) are all blue, green, or purple. The corresponding SPY's are red, brown, or purple, and if the number and kind of ligands are the same in the two geometries, as in those discussed here, the lowest energy ligand field band occurs at lower energy in the case of the TBP. When we go to the mixed cyanide-arsine, however, the result is that the lowest energy absorption maximum is found in the SPY spectrum. The lowest energy band in the SPY is of relatively low intensity (for $Ni(diars)_2CN^+$, ϵ = 355, in acetonitrile at 300°K). If we compare the most intense ligand field bands in the two compounds, we find that for cyanides and halides, the intense absorption at lower energy is found in the TBP. It is worth examining briefly the basis of these band position results.

On the basis of the simple ligand-field picture, we would expect replacing chloride by cyanide in the TBP system studied here to raise the $a_1(z^2)$ level and raise the energy of the first ligand field band, which is assigned as $^1A_1 \rightarrow {}^1E$ $(xy, x^2 - y^2 \rightarrow z^2)$. Making the same replacement in the SPY case should also raise the $a_1(z^2)$ level, which

should lower the energy of the first ligand field band, assigned as $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$). (Actually, this band exhibits a small shift in the opposite direction, as mentioned before.) The net result, determined experimentally, is to reverse the positions of the lowest energy ligand field bands in the SPY and TBP. Replacing chloride by cyanide acts to increase the energy of the intense ligand field band for both the SPY ($xz,yz \rightarrow x^2 - y^2$) and the TBP ($xy, x^2 - y^2 \rightarrow z^2$). Cyanide is a good π-acceptor and thus lowers the energy of the e(xz,yz) level in the SPY, and a good σ-donor and raises the energy of the $a_1(z^2)$ level in the TBP. The intense band shows a greater shift in the TBP, but no reversal occurs. The result is that for the intense ligand field band in both the cyanides and the halides, SPY > TBP. A comparison of band positions and extinction coefficients for $Ni(TAA)X^+$ and $Ni(diars)_2X^+$ is given in Table VI.

There are a number of compounds of geometry intermediate between the two limiting forms. This is undoubtedly due to the relatively low barrier to interconversion between these two geometries. It would be of interest to examine the ligand-field spectra of some of these compounds to determine whether the intermediate structure is maintained in solution, at room temperature and 77°K, and to determine the spectral characteristics which these structures exhibit. An application of the ideas discussed here is described in Appendix III.

Table VI

Comparison of Ligand-Field Bands in TBP and SPY Complexes[a]

$Ni(diars)_2Cl^+$	$Ni(TAA)Cl^+$	$Ni(diars)_2Br^+$	$Ni(TAA)Br^+$	$Ni(diars)_2CN^+$	$Ni(TAA)CN^+$
18,030 (Sh 65)	15,600 (3900)	17,610 (80)	15,100 (3720)	19,170 (400)	21,230 (5450)
22,080 (1530)	20,790 (Sh 120)	21,840 (1820)	19,800 (Sh 170)	26,415 (1730)	27,625 (360)
26,285 (190)		26,650 (Sh 110)			

[a]All measurements at 77°K in 2-methyltetrahydrofuran-ethanol or methanol. $\bar{\nu}$ $cm.^{-1}$ ($\epsilon, \ell.mole^{-1}cm.^{-1}$).

A P P E N D I C E S

APPENDIX I

NUCLEAR MAGNETIC RESONANCE STUDIES OF DYNAMIC PROCESSES IN DIARSINE COMPLEXES

Nuclear magnetic resonance measurements as a function of temperature have been carried out on a number of cobalt(III), nickel(II), and palladium(II) complexes of diarsine. Line-broadening of the resonance which corresponds to the methyl groups in the coordinated ligand occurs at low temperature, but splitting of the resonance has not been observed. This behavior is taken as evidence of structural instability in all of the complexes studied, and exchange of X in the five-coordinate $M(diars)_2X^+$ (M=Pd,Ni,X=Cl,Br,CN) complexes.

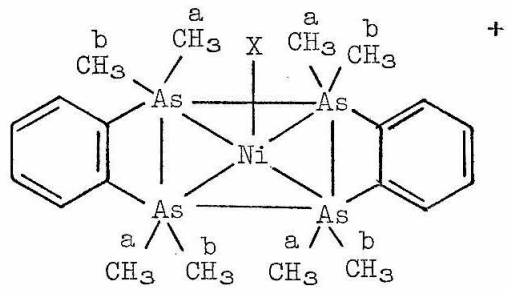
The nuclear magnetic resonance (nmr) spectrum of diarsine shows one sharp signal at δ = 1.14 ppm arising from the four equivalent methyl groups. Diamagnetic complexes of diarsine exhibit this resonance also, with the position shifted to higher fields (for $Ni(diars)_2Cl_2$ in CH_3OH, δ = 1.84 ppm). We have studied the nmr spectra of a number of four-, five-, and six-coordinate diarsine complexes of nickel(II), palladium(II), and cobalt (III) as a function of temperature. Studies on the five-coordinate complexes reveal the existence of a process involving rapid exchange of the axial ligand(X). There is also evidence for some structural instability in all of these diarsine complexes. At low temperature, significant broadening of the resonance arising from the methyl protons is observed, but separate lines corresponding to distinct species are never resolved.

Experimental. The complexes were all prepared according to standard techniques (56,104,141,142). Microanalyses were carried out on all compounds, and good agreement with calculated values was obtained. Spectroquality solvents (MCB) were used wherever possible. Spectroquality nitromethane (MCB) was found to show weak impurity peaks in the nmr, presumably due to higher nitroalkanes. Standard methods of purification did not eliminate this problem (132). An elaborate fractional distillation appeared to be necessary to completely purify this solvent, and was not carried out. All nmr measurements were made on the Varian A-60A spectrometer, or the Varian A-56/60A, which was equipped with a standard variable temperature accessory, Varian model V-6040. The Varian A-56/60A instrument is in the laboratories of Prof. John D. Roberts at Caltech. Samples were pipetted into precision-ground, 5-cm. Varian nmr tubes. In some of the measurements the signal was augmented by using a computer of average transients (CAT), Varian Associates Model C-1024, to scan the region of interest repeatedly.

Results and Discussion. The compounds studied fall into three classes: the four-coordinate nickel complex, the five-coordinate nickel and palladium complexes, and the six-coordinate cobalt complexes. The nmr spectra of these complexes, and of the ligand diarsine itself, have been measured from room temperature down to -60°C or below. The positions of solvent peaks have been used as an internal standard. The position of the resonance is not so important as the behavior of the lineshape as a function of temperature, however.

The four-coordinate nickel(II) and palladium(II) complexes are thought to be square planar and consistent with this, one sharp unsplit

methyl resonance is observed (δ = 2.01 ppm) for $Ni(diars)_2(ClO_4)_2$ in dimethylformamide (DMF). The five-coordinate complexes of nickel and palladium are believed to be square pyramidal (Part II, Chapter III), and so it is expected that two non-equivalent types of methyl groups should be observed, a and b, those on the side of the $NiAs_4$ square plane



opposite X, and those on the same side of the square plane as X. The room temperature nmr of the five-coordinate species of the form $[M(diars)_2X]^+$ (M=Pd,Ni;X=Cl,Br,I,CN) show one sharp singlet arising from the methyl groups. Integration of this peak and that corresponding to the aromatic protons shows the areas to be in the ratio of approximately 3:1 as found for diarsine, and as expected in this case if all the methyl protons are contained in this resonance. The only reasonable explanation for this result is that rapid exchange of the fifth ligand (X) is occurring in these complexes. For one sharp signal to appear in the nmr spectrum, the rate of the exchange process would have to be $\gtrsim 10^4$-10^5 sec.$^{-1}$ (143). In view of the observed rate of exchange of axial water molecules in square-planar copper(II), which is 2×10^8 sec.$^{-1}$ (144), a rate of 10^4-10^5 sec.$^{-1}$ in this case seems not unlikely.

In order to obtain more definitive evidence for this exchange process, it was decided to measure the nmr spectrum of the five-

coordinate complexes at low temperature. The exchange process should be slower at low temperature, hopefully slow enough (Rate $\lesssim 10^4$ sec.$^{-1}$) that distinct resonances from the non-equivalent methyl groups would appear. This technique has been used with success in many exchanging systems (145,146). Methanol (f.p. -98°C) was found to be an appropriate solvent for this study. Measurements of the methyl resonance from the complex, and the ^{13}C satellites of the methyl resonance from methanol were carried out from -40°C to -90°C. These measurements were made on the compounds listed in Table I, and while substantial broadening of the methyl resonance of the complex relative to that of methanol was observed, in no case was it possible to resolve a splitting of the signal, arising from non-equivalent methyl groups. Broadening of the solvent resonance at low temperature does occur, presumably as a result of the increased viscosity, but the broadening of the solute peak is considerably greater.

In order to make certain that the broadening observed was not simply due to some conformational effect exhibited by the diarsine molecule alone, the nmr spectrum of diarsine in methanol was measured from 40° to -90°C. The broadening of the methyl resonance of diarsine was seen to occur to the same extent as the broadening of the solvent resonance. This indicates that the broadening observed in the low temperature nmr of the metal complexes in fact does not arise from some conformational effect exhibited by the diarsine molecule alone.

The behavior of a number of complexes which were not expected to exhibit any kind of X-exchange process was observed, and all of these showed line broadening at low temperature, of the same type as exhibited

by the five-coordinate complexes. The four-coordinate $Ni(diars)_2(ClO_4)_2$ in DMF is suspected of actually behaving as a five-coordinate complex, with solvent loosely bound in a fifth position, in view of the ease with which the $[Ni(diars)_2]^{2+}$ unit adds a fifth ligand. For this reason, we did not use this rather obvious reference compound for the purpose of calibration. The six-coordinate cobalt(III) complexes, $Co(diars)_3(ClO_4)_3$ and $[Co(diars)_2Cl_2]Cl$, however, are not expected to undergo any kind of X-exchange process. The low temperature nmr spectra of both of these complexes show broadening of the methyl resonances to a greater extent than the solvent line broadening. The same effect is observed in the low temperature nmr of the five-coordinate $Ni(diars)(triars)^{2+}$. A likely explanation of these results is that the molecular framework is structurally non-rigid in these diarsine complexes, and that there are more than one possible static conformation which give rise to non-equivalent methyl groups. An examination of a CPK space-filling model of the $Co(diars)_2Cl_2^+$ molecule, for example, shows that, assuming approximately tetrahedral bond angles about arsenic, there are two non-equivalent methyl groups in the molecule, due to the apparent "chair-like" conformation of the molecule. This result is borne out by available crystal structural data (19,20,57). The bis-complex of 1,8-naphthalenebisdimethylarsine with nickel(II) exhibits two isomers, thought to be of the "chair" and "boat" forms (147), in accord with this interpretation. Apparently there is a low energy barrier separating the two forms, and at room temperature they equilibrate rapidly. At low temperature the process slows down, and line broadening occurs. The extent of the line broadening at low temperature is not greatly different in

the five- and six-coordinate complexes. This indicates that the conformational equilibration process occurs either more slowly than or at approximately the same rate as the X-exchange process.

The proposed rationalization appears to be the most reasonable for the data presented. However, it is unfortunate that the low temperature measurement does not show resonances from two non-equivalent methyl groups. The unequivocal proof of the proposed mechanism really depends upon identification of non-equivalent resonances. For the six-coordinate complexes, two separate lines should appear due to the freezing out of the conformational exchange. In the spectra of the five-coordinate complexes, however, four lines are expected at sufficiently low temperature, because the combination of the conformational distortion with the presence of halide should lead to four different types of methyl groups in the complex. If the explanation is correct, carrying out the measurement at sufficiently low temperature in the proper solvent should bring about splitting of the signal. The lowest temperature attained in this study was -100°C, using C_2D_5OD as solvent. Unfortunately, the deuterated solvent seems to freeze at a higher temperature than ethanol, and from the standpoint of viscosity broadening is a less suitable solvent than methanol, which only permits measurement down to -90°C. The results indicate that -100°C is not a low enough temperature to allow detection of the non-equivalent methyl groups.

An alternative explanation of the data which should be considered is that of rapid diarsine-exchange. This could occur along with X-exchange or alone, and would satisfactorily account for the observed results.

Another possible approach to the X-exchange problem would be to study the trimethyl phosphite adduct of $Pt(diars)_2^{2+}$. We have found that $Ni(diars)_2[P(OCH_3)_3]^{2+}$ forms readily, and the corresponding platinum complex should not be difficult to obtain in solution. This system could be studied by ^{31}P and proton nmr, and the Pt-P and Pt-H coupling should provide additional information about the X-exchange process.

Table I

Compounds Examined in nmr Study

Room temperature and low temperature:	$Ni(diars)_2Cl_2$
	$Pd(diars)_2Cl_2$
	$[Pd(diars)_2Cl]ClO_4$
	$Ni(diars)(triars)[B(C_6H_5)_4]_2$
	Diarsine
	$Co(diars)_3(ClO_4)_3$
	$Co(diars)_2Cl_3$
Room temperature only:	$Ni(diars)_2(ClO_4)_2$
	$[Ni(diars)_2CN]ClO_4$
	$Ni(diars)_2Br_2$

APPENDIX II

LINKAGE ISOMERIZATION IN $Ni(diars)_2CNS^+$

While solid $[Ni(diars)_2CNS]Y$ ($Y=B(C_6H_5)_4, ClO_4$) exhibits one slightly split band at the carbon-nitrogen stretching frequency, solutions of these compounds exhibit two bands. This result is taken as evidence of ligand isomerization in this system. Additional experimental evidence is offered in support of the assignment of these two bands to the N- and S-bonded thiocyanate complexes.

There has been considerable interest in recent years in complexes of transition metal ions with the ambidentate ligand, thiocyanate (148,149). A large number of complexes have been prepared containing either the N-bonded or the S-bonded form. In a few cases, both isomers of a given complex are known (149,150), and there are also examples of complexes thought to contain both the N-bonded and S-bonded ligands in a single molecule (151). Infrared spectroscopy has proved to be a very useful tool in characterizing thiocyanate complexes. Turco and Pecile have worked out empirical rules for distinguishing N- from S-bonded thiocyanate in complexes, on the basis of the position of ν_{C-S} (152), the C-S stretching frequency, and the integrated intensity of ν_{C-N} (153), the C-N stretching frequency. There have been a number of attempts to come up with generalizations concerning the metal ion and the other ligands present in the complex which would explain the preference for N- or S-bonded thiocyanate in particular complexes (154). While some progress has been made in this area, there seems to be no clear-cut rule which is universally correct.

We have carried out an infrared spectral study of $Ni(diars)_2CNS^+$ in the solid and in solution. Our results indicate that while both the perchlorate and tetraphenylborate salts of this complex cation exist in only one of the isomeric forms (probably N-bonded), both linkage isomers are present in solution.

Experimental. The preparation of $[Ni(diars)_2CNS]ClO_4$ has been described in Part II, Chapter II. $[Ni(diars)_2CNS][B(C_6H_5)_4]$ was readily prepared by mixing a solution of sodium tetraphenylborate in methanol with a methanol solution of $[Ni(diars)_2CNS]ClO_4$. The precipitate formed was washed many times with methanol, in which it is very slightly soluble, and recrystallized from a dichloromethane-methanol solvent mixture to give dark red crystals.

Anal. Calcd. for $C_{45}H_{52}As_4$ NSBNi: C, 53.61; H, 5.12; As, 29.75.

Found: C, 54.55; H, 5.27; As, 29.60.

Spectroquality grade dichloromethane, acetonitrile, and methanol (MCB), and reagent grade dimethylsulfoxide (Baker and Adamson) were used as solvents in the infrared and uv-visible spectral studies. Infrared measurements were made on a Perkin-Elmer Model 225 grating spectrophotometer, using potassium bromide plates for the mull spectra, and matched 1.00 mm. cells with calcium fluoride windows for solution measurements. The Beer's law determination for the visible spectrum was carried out using Suprasil square cells with solid silica inserts which give pathlengths of 0.01, 0.03, 0.10, 0.30, and 1.00 cm. Uv-visible spectra were measured as described previously.

Results and discussion. The infrared spectrum of solid

$[Ni(diars)_2CNS]Y$ ($Y=ClO_4, B(C_6H_5)_4$) as a Nujol mull exhibits one slightly split band in the thiocyanate region, with the components appearing at 2061 and 2069 $cm.^{-1}$. In solution, however, the infrared spectrum of $Ni(diars)_2CNS^+$ in this region exhibits two distinct bands, at 2060 and 2090 $cm.^{-1}$. The detailed results in a number of solvents are given in Table I. Since the five-coordinate complex contains only one -CNS group, only one value of ν_{C-N} is expected. The small splitting of this band ($\Delta \bar{\nu}=8$ $cm.^{-1}$) observed in the spectrum of the solid is most likely due to crystal packing effects. In solution, the two bands observed must arise from two distinct types of thiocyanate. The possible explanation for the existence of two bands seem to be as follows: (1) both N-bonded and S-bonded isomers of $Ni(diars)CNS^+$ are present in solution (2) both free and bound thiocyanate are present, due to dissociation of the complex (3) bridging thiocyanate is present in addition to either the free ion or one of the bonded isomers.

We examine the least interesting possibility (2) first, that of dissociation of the complex, which would give rise to two infrared bands in solution.

$$Ni(diars)_2CNS^+ \underset{}{\overset{K}{\rightleftharpoons}} Ni(diars)_2^{2+} + SCN^-$$

Free thiocyanate exhibits a band at ~ 2060 $cm.^{-1}$ (153), which is approximately the same frequency as observed for the split band in the solid $[Ni(diars)_2CNS]Y$, and for one of the bands in solution. The visible absorption spectrum of $Ni(diars)_2^{2+}$ is well known (99) and if dissociation of $Ni(diars)_2CNS^+$ occurs, this spectrum should appear. The visible absorption spectra of $[Ni(diars)_2CNS]Y$ in the solid and in organic sol-

vents ($C > 10^{-4}$ M.) are very different from that of the four-coordinate $Ni(diars)_2(ClO_4)_2$, and are infact similar to the chloride and bromide, which are five-coordinate. These data have been presented in Part II, Chapter 3. Also, the molar conductivity of $[Ni(diars)_2CNS]NCS$ in nitromethane ($C=10^{-3}$ M.) is essentially the same as that for the corresponding chloride, bromide, and iodide, and is quite different from that exhibited by $Ni(diars)_2(ClO_4)_2$ (99).

The infrared spectra have been measured in organic solvents, with $C > 10^{-3}$ M. in every case, and so there seems to be considerable evidence against explanation (2). In order to check for dissociation, a Beer's law determination was carried out simultaneously in the infrared and visible spectrum. Over a range of concentrations from 1.5×10^{-3} M. to 2.2×10^{-2} M. $[Ni(diars)_2CNS]ClO_4$ is acetonitrile, Beer's law for the main visible absorption band (λ_{max}=474 nm) is obeyed to $\pm$ 1.4%, which is within experimental error. The behavior of the infrared bands is not so good as this, one band showing deviations of $\pm$ 6%, the other deviations of $\pm$ 8% for the three solutions measured. These figures are close to the limits of the experimental error. Unfortunately, one solution was too dilute and one too concentrated for accurate measurement of the percent transmittance. The important point to be noted concerning this experiment is that the ratios of the absorbance at one peak maximum to the absorbance at the other maximum for five different concentrations show a standard deviation of only $\pm$ 1% (see Table I). If a dissociation process obeying the law of mass action were in force, there should be a change in this ratio by a factor of four over the fifteenfold concentration range employed here. The constancy of this ratio

clearly indicates that dissociation is not occurring in the concentration range of this study.

Turning to the other suggested explanations, the possible existence of any reasonable thiocyanate-bridged complex is apparently ruled out by the conductivity measurement reported by Nyholm and coworkers (99). The conductivity of the nitromethane solution of $[Ni(diars)_2CNS]NCS$ is very close to those of the chloride, bromide, and iodide, which are monomeric, 1:1 electrolytes. Also, the positions of the two $\tilde{\nu}_{C-N}$ bands in the infrared are rather low for bridging thiocyanate groups, though these positions in themselves are not sufficient evidence to rule out bridging thiocyanate (153). We conclude that the two bands in the infrared solution spectrum of $Ni(diars)_2CNS^+$ correspond to the two linkage isomers, the N-bonded form (presumably $\tilde{\nu}$ = 2060 cm.$^{-1}$) and the S-bonded form ($\tilde{\nu}$ = 2090 cm.$^{-1}$).

It has been found in a number of cases that the S-bonded isomer exhibits $\tilde{\nu}_{C-N}$ at slightly higher energy than the N-bonded isomer (153). The region of the spectrum (~ 700-850 cm.$^{-1}$) which contains $\tilde{\nu}_{C-S}$ is obscured by diarsine absorption. This is unfortunate, since $\tilde{\nu}_{C-S}$ is used to distinguish the N-bonded from S-bonded thiocyanate. The observed difference in half-widths of the bands (acetonitrile solution) is consistent with the majority of the known cases (152), the band arising from the supposed S-bonded form being less broad ($\Delta \tilde{\nu}_{\frac{1}{2}}$ = 9 cm.$^{-1}$) than the band from the N-bonded form ($\Delta \tilde{\nu}_{\frac{1}{2}}$ = 25 cm.$^{-1}$). Because of the similarity in position of the solid band with the 2060 cm.$^{-1}$ band in solution, it is proposed that the compound is N-bonded in the solid. It would be worthwhile to carry out a crystal structure determination on this com-

pound to test this conclusion.

The ratio of the absorbances at the peak maxima in solution is a measure of the relative amounts of the two isomers present in solution. Assuming that the band at ~ 2060 cm.$^{-1}$ is due to the N-bonded complex and that at ~ 2090 cm.$^{-1}$ is due to the S-bonded complex, A_{2060}/A_{2090} should increase with the proportion of the N-bonded form. The infrared spectrum of $Ni(diars)_2CNS^+$ has been measured in three different solvents, and the absorbance ratios are given below:

Solvent	A_{2060}/A_{2090}	Dielectric Constant of Solvent[a]
Dichloromethane	2.5	9.08
Acetonitrile	1.82	37.5
Dimethylsulfoxide	~ 1.4	

[a]From Ref. 155.

Dichloromethane apparently favors the N-bonded isomer more than the other solvents; the proportion of the S-bonded form is greatest in dimethylsulfoxide. This result is in accord with the solvent-dependent isomerization of $Co(CN)_5CNS^{3-}$ reported by Gutterman and Gray (150). They found that in aqueous solution the S-bonded form of that complex predominates and in dichloromethane, the N-bonded form is favored. Their rationalization of the effect was that the "hard" nitrogen end of the thiocyanate ligand should be better stabilized by the strongly polar solvent, water, causing the S-bonded isomer to be favored. In the less polar dichloromethane, the polarizable sulfur end is better stabilized, and the N-bonded form is favored. The results tabulated above clearly indicate the same trend: increasing solvent polarity decreases A_{2060}/A_{2090}, indi-

cating increasing relative stabilization of the S-bonded isomer.

Because the extinction coefficients of the infrared bands due to the pure N- and S-bonded forms are not known, the absorbance ratios cannot be used to determine the relative amounts of the two isomers. This determination could be made if a solvent were found in which only one of the isomers is present. It might be possible to obtain a solution containing only one isomer by measuring these solutions at low temperature, since the equilibrium should show some temperature-dependence. It was noted earlier that the integrated intensities of $\tilde{\nu}_{C-N}$ for S- and N-bonded thiocyanate complexes are quite different, and serve to characterize these isomers (153). By assuming reasonable values for the integrated intensities of $\tilde{\nu}_{C-N}$ for the N-bonded complex, the S-bonded complex, and for free thiocyanate, it is possible to assign the two bands in different ways and to calculate possible percentage compositions. Using the data tabulated by Pecile (153) as "reasonable" values for the product $(\epsilon_{max})(\Delta \tilde{\nu}_{\frac{1}{2}})$, which approximates the integrated intensity, we have, for a wide variety of complexes and solvents:

	$\frac{(\Delta \tilde{\nu}_{\frac{1}{2}})(\epsilon_{max})}{}$
free NCS^-	$14{,}600 \pm 5000$
M-NCS	$29{,}500 \pm 7000$
M-SCN	$5{,}500 \pm 6000$

For $Ni(diars)_2CNS^+$ in acetonitrile solution, we have measured the integrated intensities of $\bar{\nu}_{2060}$ and $\bar{\nu}_{2090}$ as follows:

	$\langle (\Delta \tilde{\nu}_{\frac{1}{2}})(\epsilon_{max}) \rangle$
$\bar{\nu}_{2060}$	17,900 ± 1500
$\bar{\nu}_{2090}$	3,500 ± 400

For these values of the integrated intensities, it is clear that the most reasonable assignment for the two bands in the spectrum of $Ni(diars)_2CNS^+$ is

ν_{2060} : ν_{C-N} due to $Ni(diars)_2NCS^+$

ν_{2090} : ν_{C-N} " " $Ni(diars)_2SCN^+$.

If we eliminate from consideration the possible presence of free NCS^-, the intensity data points clearly to this assignment. There are, of course, a variety of ϵ's and percentage compositions which give agreement with the observed values of $(\epsilon_{max})(\Delta \tilde{\nu}_{\frac{1}{2}})$ for ν_{2060} and ν_{2090}. A reasonable example is a 55%/45% mixture of the N-bonded and S-bonded isomers. In this case, we would have $(\Delta \tilde{\nu}_{\frac{1}{2}})(\epsilon_{max})$ = 32,500 for the N-bonded form and 7800 for the S-bonded form, both of which fall within the limits of the data collected by Pecile.

We report here the first instance of thiocyanate S-bonded to nickel, and one of the few cases of linkage isomerization for a first row transition metal ion. Using the reasoning employed by Ahrland (154) in discussing the preferred mode of coordination for the thiocyanate ligand, it is noted that highly polarizable, "soft," or "Class b" donor ligands such as arsines must be present in order to induce thiocyanate to S-bond to the "hard" metal ion, nickel(II). For example, a crystal structure determination has been carried out on the four-coordinate nickel complex, [Ni(Et_4dien)NCS]I (155), which was found to be N-bonded. The ligand Et_4dien has "hard" nitrogen donor atoms. The presence of the

two isomers in solution indicates that the case of $Ni(diars)_2CNS^+$ is just at the change-over point for favoring N- or S-bonding of thiocyanate. It would be of interest to examine other complexes of nickel(II) with phosphines, arsines, and thiocyanate to obtain N- and S-bonded isomers, and perhaps to elucidate some of the steric and electronic factors governing the phenomenon of linkage isomerization. It is worth noting that one of the complexes thought to contain both N- and S- bonded thiocyanate in the same molecule is a mixed arsine-phosphine complex of palladium(II) (151).

Table II

Infrared Data on $Ni(diars)_2CNS^+$

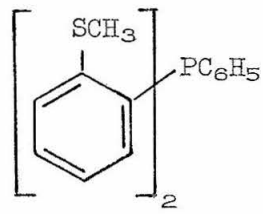
Solvent	$\bar{\nu}$	A	A_{2060}/A_{2090}
Nujol mull	2069 cm.$^{-1}$ 2061		
Dimethylsulfoxide	2087 2056	.80 1.14	1.4
Dichloromethane	2088 2061	.114 .266	2.34
		.078 .215	2.76
Acetonitrile	2090 2060	.241 .427	1.77
		.059 .111	1.88
		.233 .424	1.82
		.780 1.41_2	1.81
		.137 .250	1.83

APPENDIX III

EQUILIBRIA INVOLVING VARIOUS FOUR- AND FIVE-COORDINATE COMPLEXES OF NICKEL(II)

The five-coordinate complexes of nickel(II) halides with bis(o-methylthiophenyl)-phenylphosphine (DSP) have been found to exhibit a number of changes in structure as a function of temperature. The electronic spectra of solutions of the bromide and iodide have been measured in a number of different solvents and at different temperatures. The spectral results are discussed in relation to the possible four-, five-, and six-coordinate species which could be present.

The preparation and characterization of a number of transition metal complexes with the terdentate, heavy-donor ligand bis(o-methylthiophenyl)-phenylphosphine (DSP) has been carried out by Meek and



(DSP)

coworkers (108). Electronic spectral measurements on the five-coordinate complexes of nickel(II) with this ligand, $Ni(DSP)X_2$ (X=Cl,Br,I) left some uncertainty concerning the coordination geometry of these complexes. More recently, a crystal structure determination of $Ni(DSP)I_2$ (21) has shown that this compound exhibits a nearly regular square pyramidal geometry. It was thought that measurement of the electronic spectra of some of the $Ni(DSP)X_2$ complexes in solution at low temperature might help clear up the ambiguity originally present in the electronic spectra. This system should also provide a good test case for the

proposed empirical rules for determining the coordination geometry of five-coordinate complexes discussed earlier (Part II, Chapter 3).

Experimental. All spectral measurements have been carried out using analyzed samples of $Ni(DSP)X_2$ (X=Br,I), kindly supplied by Prof. D. W. Meek of the Ohio State University. Solvents for spectral measurements were spectroquality (MCB), and the tetra-n-butylammonium bromide and iodide were Eastman white label reagents. The following solvent mixtures were used for spectral measurements at low temperature: 2:1 2-methyl-THF/ethanol (EM); 3:1 2-methyl-THF/propionitrile (PM); 3:1 2-methyl-THF/dichloromethane (DM). Spectral measurements at 77°K were carried out as previously described (Part II, Chapter 2). Measurements at intermediate temperatures between 300 and 77°K were carried out using the same quartz Dewar and cell holder assembly. Constant temperatures were achieved by blowing a continuous stream of nitrogen gas, cooled by passing through a copper coil submerged in a liquid nitrogen bath, into the quartz Dewar. The temperature at the cell was monitored using a copper-constantan thermocouple and a Leeds & Northrup millivolt potentiometer.

Results and discussion. The electronic spectrum of $Ni(DSP)X_2$ (X=Br,I) has been measured in a variety of solvents at 300°, 77°K, and intermediate temperatures. Dissociation of X^- is seen to occur at room temperature in acetonitrile solution, but not in dichloromethane. The equilibrium in acetonitrile may be pictured in this way

$$Ni(DSP)X_2 \rightleftharpoons Ni(DSP)X^+ + X^-$$

$$\uparrow\downarrow ?$$

$$Ni(DSP)(solvent)_x^{2+} + X^-$$

If a solution of $Ni(DSP)X_2$ in CH_3CN is diluted 10:1 and placed in a 10 cm. absorption cell, the absorbance at λ_{max} decreases sharply. Upon addition of $[(\underline{n}\text{-}C_4H_9)_4N]X$, the absorbance is restored to its original value. This effect is easily observed visually. No new absorption bands appear in the spectrum of either compound when dilutions are made or stoichiometric amounts (1:1) of $AgNO_3$ added. It has not been determined whether the equilibrium involves dissociation of one or two halide ions. However, conductivity work by Meek indicates that in DMF, $Ni(DSP)Br_2$ at $\sim 10^{-2}$ is almost entirely dissociated into $Ni(DSP)(Solvent)_x^{2+} + 2\ Br^-$ (108). Also, the absence of an absorption band attributable to $Ni(DSP)X^+$ in the spectrum of the dissociated compound disposes one to think more in terms of complete dissociation of halide. Solutions of $Ni(DSP)Br_2$ are stable on standing, while solutions of $Ni(DSP)I_2$ in polar solvents turn yellow irreversibly in a matter of hours, due to formation of I_3^- (λ = 361 nm, 291 nm).

On cooling, the spectra of the two compounds behave rather differently.

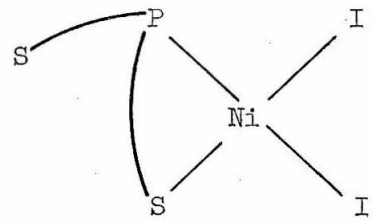
<u>Ni(DSP)I_2</u>. In dichloromethane solution, the absorbance of the intense band at 595 nm increases on cooling, and a definite shoulder is developed on the high-energy side (λ = 534 nm, Shoulder; T ~ 185°K). In EM or PM, the absorbance of the intense band (λ_{max} = 607 nm) decreases drastically on cooling, and a new band appears at higher energy (λ_{max} =

532 nm; T=77°K). Also, a new shoulder appears at 468 nm. On warming, the original spectrum reappears. Added iodide (0.1 M.) has no effect on the observed temperature dependence of the spectrum.

It is clear that in dichloromethane no structural changes occur on cooling. The absorbance of the main band increases, and a shoulder is partially resolved, both observations consistent with the decrease in bandwidths which occurs on lowering the temperature of any absorbing solution. The observed spectrum is consistent with expectation for a square pyramidal complex, and is different from that expected for a trigonal bipyramid. In the latter case, one does not expect to see resolution of a shoulder on the main band, but rather an increase in the symmetry of the band at low temperature. It has been noted (Part II, Chapter 3) that the position of the intense band in the spectrum of a TBP complex falls at substantially lower energy than that for the SPY complex, assuming ligands of about the same ligand field in the two cases. The band maximum for $Ni(TSP)I^{+}$ appears at 15,060 $cm.^{-1}$ (157) (300°K, in dichloromethane) as compared with 16,810 $cm.^{-1}$ in this case. This is consistent with expectation for square pyramidal $Ni(DSP)I_2$.

The sharp decrease in the intensity of the bands corresponding to the square pyramidal complex, which occurs at low temperature in EM, indicates that the amount of this species present has decreased. The new species which replaces it must give rise to the absorption band at 468 nm. The position of this band is correct for a four-coordinate, square planar complex. For example, the four-coordinate $Ni(SP)_2(ClO_4)_2$ exhibits a band at 21,600 $cm.^{-1}$ in dichloromethane at 300°K (108), as compared with the band position of 21,368 $cm.^{-1}$ in EM at 77°K observed

in this case. Because added iodide does not affect the spectrum, it is apparent that the four-coordinate species does not originate by dissociation of I^-. Perhaps one of the "teeth" of the tridentate ligand becomes detached, to give a four-coordinate complex of the form



Ni(DSP)Br_2. In dichloromethane solution, the absorbance of the intense band at 541 nm steadily decreases on cooling, and a definite shoulder begins to emerge on the low energy side of the band (λ = 650 nm, T ~ 185°K). Both of these effects are opposite to the results obtained with Ni(DSP)I_2. The compound is not very soluble in EM, but by adding a small amount of dichloromethane, the solubility may be increased. In this solvent, the band at 544 nm (300°K) disappears at low temperature, and an additional shoulder appears around 380 nm. This solution is yellow at 77°K. In PM or DM, the band at 544 nm (300°K) disappears at low temperature, and a weak new band appears at 650 nm (77°K). These solutions are pale green at 77°K. In CH_3CN at 300°K, there is a weak shoulder at 615 nm which varies with (Br^-) in about the same way as does the intense band at 540 nm. Added bromide does not appear to affect the observed temperature dependence of the spectrum. Complete spectral results for this compound and Ni(DSP)I_2 are collected in Table I.

The decrease in absorbance on cooling, observed for the intense band in the spectrum of this compound in dichloromethane, is not the expected result, as was indicated above. The decrease of the band, and the appearance of the shoulder at 650 nm, indicates that a new species is being formed, at the expense of the original one. The original complex is assumed to have square pyramidal geometry, by analogy with $Ni(DSP)I_2$. Additional evidence for this explanation of the intensity decrease of the main band with decreasing temperature is given by the fact that at 77°K in PM or DM, the main band has disappeared, and the new band at 646 nm is present. The position of this new absorption ($\tilde{\nu}$ = 15,480 $cm.^{-1}$ in DM, T = 100°K) is in the correct region for assignment as the prominent band in the spectrum of $Ni(DSP)Br_2$ with a TBP structure (for $Ni(TSP)Br^+$, $\tilde{\nu}$ = 15,150 $cm.^{-1}$ in dichloromethane, T = 300°K) (157). The low intensity of the 646 nm band indicates that only a fraction of the TPY complex goes to the supposed TBP form, since extinction coefficients are generally of the same order of magnitude for the intense band in the two geometries. Additional evidence for this is provided by the low temperature spectrum in EM, in which the maximum at 544 nm has disappeared but no new absorption at ~ 650 nm appears. There are new absorptions at 380 nm and 400 nm which might logically be assigned to a four-coordinate species, as postulated for the iodide. The presence of these bands in the low temperature spectrum in PM and DM indicates that some of this form, as well as the TBP, is probably present in these solutions at low temperature. There is also the possibility that the bands observed in the low temperature spectrum are due to some six-coordinate species involving DSP and

solvent, with bromide dissociated. Such complexes were detected with $Ni(Et_4dien)^{2+}$ and added pyridine or Et_4dien at low temperature (5). However, the fact that the observed bands in this case appear at low temperature using the poorly coordinating solvent dichloromethane, and not with ethanol, which is expected to coordinate better, casts doubt on this interpretation. A number of other five-coordinate species might be present in solution and give rise to the observed low-temperature spectrum. These could involve coordinated solvent, or ligands only partially coordinated. It is impossible at this point to rule out such unknown possibilities, and for this reason the interpretation given for these spectra must be regarded as tentative.

We present evidence here for the existence of temperature-dependent equilibria thought to involve both four- and five-coordinate species derived from $Ni(DSP)X_2$ (X=Br,I). It appears that both SPY and TBP structures may be involved in these equilibria for X = Br. It is not profitable at this time to speculate on the factors which might lead $Ni(DSP)Br_2$ to exhibit this isomerism and $Ni(DSP)I_2$ not to do so. It would be worthwhile to examine the analogous chloride complex which has been prepared and characterized (108), in view of the apparent tendency toward the TBP at low temperature with more electronegative X. Another possible technique for studying this system would be a temperature-dependent infrared spectral study. This could best be carried out using complexes with X = NCS, N_3, NCSe, CN, or NO_2. None of these have been reported, but it seems very likely that the first three, at least, could be readily prepared and characterized.

Table I

Electronic Spectra of $Ni(DSP)X_2$

X	Solvent	T	λ(nm)	ε or A
I	CH_2Cl_2	300°K	595	1250 .62
		185	589	.73
			s 534	.49
	EM	300°	607	1185
		77°	604	365
			532	321
			s 468	778
	CH_3CN	300°		
Br	CH_2Cl_2	300°	541	800 .76
		185°	532	.51
			s 650	.12
	EM	300°	544	.087
			s 400	
		77°	s 400	.43
			s 382	
	DM	300°	544	.46
			s 400	.68
		100°	646	.06
			s 400	.45
			s 380	.65
	PM	300°	542	
			s 396	
		77°	658	
			s 400	
	CH_3CN	300°	s 612	.08
			539	.20

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P R O P O S I T I O N S

PROPOSITIONS

I.

Magnetic circular dichroism (MCD) experiments are proposed to provide additional evidence concerning the assignment of certain bands in the electronic absorption spectra of $Ni(diars)_2X^z$ and $Ni(diars)_2^{2+}$.

II.

It is proposed to extend the experiments described in this dissertation involving the production of arsenic radical species by uv-photolysis to include organic derivatives of other Group V elements and the heavier elements of Group VI. It is further proposed to extend the spectroscopic techniques used in studying these radical species to include uv-visible absorption, infrared and Raman spectroscopy, as well as electron spin resonance (esr).

III.

Electron spin resonance (esr) experiments are proposed to help elucidate the role of the molybdenum and iron atoms in the active site(s) of the nitrogen-fixing enzyme system from Azotobacter vinelandii.

IV.

Kinetic studies are proposed to elucidate the mechanism of the oxidation and reduction reactions of the bis-diarsine complexes of nickel.

V.

Synthetic experiments under conditions approximating those thought to exist on pre-biotic Earth have succeeded in producing simple, biologically important monomers. Fragmentary reports of the use of heterogeneous solid/solution systems indicate that for certain types of reactions this approach is better than simple homogeneous systems. A study of the application of insoluble phosphate minerals in a heterogeneous system to the formation of phosphate esters under pre-biotic Earth conditions is proposed.

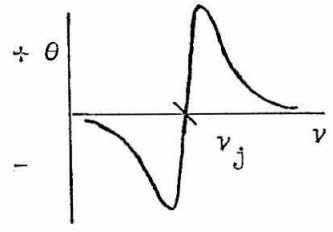
PROPOSITION I

In recent years, the technique of magnetic circular dichroism (MCD) has been found to be one more useful tool for the chemist interested in the electronic structures of transition metal complexes (1,2). In particular, MCD measurements provide direct evidence concerning the degeneracy of excited states. Measurements may be carried out in solution, with concentrations about an order of magnitude larger than appropriate for measurement of the uv-visible absorption spectrum. Although the experimental setup is not complicated, there are apparently few in operation at present. The apparatus consists of a spectropolarimeter of the type used to measure optical rotatory dispersion (ORD) and circular dichroism (CD) of optically active species, and a magnet. In much of the original work employing this technique, the magnetic field (up to 45 kilogauss) was furnished by a small superconducting solenoid which fits compactly around the sample and inside the sample compartment of the spectropolarimeter (2). More recently, a permanent magnet capable of fields up to 11 kilogauss has been used to supply the magnetic field (3).

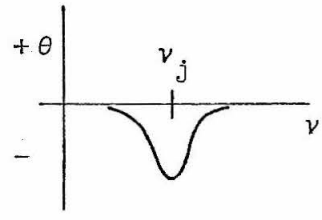
The theoretical expressions for the Faraday effect (MORD and MCD) contain three terms, A, B, and C (1). A terms arise from the Zeeman splitting of the ground or excited states, and thus can only be present when a degenerate state is involved in the electronic transition. B terms are caused by the mixing of states by the magnetic field, and C terms arise from Zeeman splitting of the ground state. C terms will be

present only if the ground state is degenerate; A terms will appear if either the ground state or the excited state involved in the transition is degenerate.

The presence of an A term is indicated by a full derivative curve in the dispersion mode, in contrast to lineshapes arising from B and C terms. Idealized lineshapes in the dispersion mode are pictured below.



A term



B or C term

ν_j is the frequency which corresponds to the band maximum in the electronic absorption spectrum.

C terms may be experimentally distinguished from B terms in that C terms are temperature dependent, while both A and B terms are independent of temperature (2).

The principal use of the MCD experiment, then, is in determining whether degenerate states are involved in observed electronic transitions. The degeneracy of the ground state of molecular species is ordinarily known from other experiments. However, in the absence of a band polarization study, the identity of excited states involved in electronic transitions is often the subject of considerable speculation. Thus the detection of A terms in the MCD experiment has proved useful in distinguishing between degenerate and non-degenerate excited states. One application of this technique was reported by Martin, who identified the $^1A_{1g} \rightarrow {}^1E_g$ ($xz,yz \rightarrow x^2 - y^2$) transition in $PtCl_4^{2-}$ by detecting an A term

in the MCD corresponding to this band (4). B terms are expected to appear for all absorption bands, and so are not of interest in characterizing absorption bands. However, the presence of B terms must be reckoned with, for a strong B term can prevent detection of an A term associated with the same transition. For this reason, failure to observe an A term is not conclusive evidence that the excited state involved is non-degenerate. This situation is observed in the MCD of the tetragonal six-coordinate complexes of cobalt(III) reported by McCaffery, et al. (5). No A terms are observed in these spectra, despite the rather well-established assignment of the lowest energy band in the spectrum as $^1A_1 \rightarrow {}^1E$.

Because of some uncertainty remaining in the assignment of the charge-transfer spectrum of $[Ni(diars)_2X]^Z$, it was thought that additional experimental evidence concerning the electronic structure would be of value. The one feature of this spectrum which remains puzzling is the band which appears near 30,000 $cm.^{-1}$, the position relatively independent of the nature of X in the series Cl, Br, I, NCS, tu. For a number of reasons detailed in Part II, Chapter 3, this band has been assigned as the electronic transition $^1A_1 \rightarrow {}^1E$ $[X(\pi) \rightarrow M(d\sigma^*)]$. An alternative assignment presented by Meek for the analogous band in the NiL_2X^+ spectra (L=SP,SeP,AP,VPP) is $P(\sigma) \rightarrow M(d\sigma^*)$ (6). The detailed assignment of this band could then be $^1A_1 \rightarrow {}^1A_1$, $^1B_1$, or ^1E. In any case, for the five-coordinate NiL_2X^+, the charge-transfer spectrum can exhibit two transitions to degenerate states, $X(\pi)$ or $P(\sigma) \rightarrow M(d\sigma^*)$. In the case of $Ni(diars)(triars)^{2+}$, X = As does not have filled π-donor orbitals, and thus can only exhibit one transition to a degenerate state, namely

$As(\sigma) \rightarrow Md(\sigma^*)$. The absorption band which has been assigned to this transition appears in every one of the $Ni(diars)_2X^+$, $Ni(diars)_2^{2+}$ complexes studied here, in the range 37-38,000 $cm.^{-1}$. If the assignment is correct, the dispersion of the MCD should exhibit an A term corresponding to this band. Also, if X is a π-donor ligand, an A term should appear at $\sim$ 30,000 $cm.^{-1}$; for the $Ni(diars)(triars)^{2+}$ and for $Ni(diars)_2^{2+}$ in acetonitrile, no A term should be observed in that region.

In addition to possibly resolving this difficulty, it is anticipated that the MCD experiment should provide evidence concerning the assignment of the relatively intense ligand field band which appears at $\sim$ 20,000 $cm.^{-1}$ in the five-coordinate species. This band has been assigned as $^1A_1 \rightarrow {}^1E$ $(xz,yz \rightarrow x^2 - y^2)$, and so should exhibit an A term in the MCD spectrum. The assignment of the corresponding band in the spectrum of the four-coordinate $Ni(diars)_2^{2+}$ is perhaps less firm, and so identification of the position of the transition to the degenerate ligand field excited state would be even more important in that case.

It is possible that one might not obtain positive results from this experiment. However, recent reports have been rather encouraging. Recent work on the MCD of $M(CN)_4^{2-}$ (M=Ni,Pd,Pt) has been reported independently by Mason (3) and Schatz (7). The dispersion of the MCD shows very strong A terms for these square-planar complexes. It has also been reported that better separation of bands is obtained in the MCD than in conventional uv-visible absorption spectra (3).

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PROPOSITION II

The production by uv-irradiation of a number of arsenic-containing radicals and measurement of their esr spectra have been reported in Part I, Chapter 3 of this dissertation. The radicals produced are thought to be of two kinds, arsine radical cations and uncharged radicals containing divalent arsenic. Production of the radical species is achieved by uv-photolysis of a frozen solution ($T \leq 96°K$) of the parent substituted arsine. Normally, irradiations have been carried out in the esr spectrometer cavity so that the esr spectrum can be measured during or soon after irradiation.

Esr results have been reported for a number of organic sulfur-containing radicals (1,2) and two organic selenium-containing radicals (3). While a few radical cations containing sulfur have been reported, most of the sulfur-containing radicals and both selenium radicals are of the form R-Q· (Q=S,Se). The characteristics of these spectra have been discussed in Part II, Chapter 3. Gordy and coworkers have reported the production of PH_2, PD_2, and phosphorus and arsenic atoms by γ-irradiation of phosphine and arsine at 4°K, and have measured the esr spectra of these species at low temperature (4). They have also reported esr results on γ-irradiated Group IV hydrides (4). In the latter experiments, they detected the presence of CH_3, SiH_3, GeH_3, and SnH_3. These species exhibit axially symmetric g-tensors with very small deviations from the free-electron value. Hyperfine splitting due to the Group IV element was observed only in the case of SiH_3 ($^{29}Si, I=\frac{1}{2}$; Nat. abundance=

4.7%), with a value of $\langle A_{Si} \rangle$ = 266 G. There has also been a certain amount of esr work done involving organic anion radicals involving phosphorus. These radicals have been produced by mixing solutions of substituted phosphines or phosphine oxides with potassium metal. The radicals detected are thought to be of the form (R_2PK^-) (5,6).

In view of the success of our experiments in producing arsenic radicals, it is expected that results of a similar nature might be obtained using aromatic or aliphatic stibines and bismuthines. It is also considered likely that low-temperature uv-photolysis of organic sulfur and selenium-containing compounds should yield interesting results. Before proceeding with more concrete proposals, it would be well to point out one problem which does restrict the usefulness of this technique somewhat. The problem is that photooxidation involves transfer of an electron from the parent molecule of interest to a molecule of solvent which in turn breaks down to yield a radical with a characteristic, highly split esr signal. This signal is centered at g = 2.00, and is often the most intense resonance in the spectrum. At the signal levels necessary to observe the arsine radical resonances in detail, it obscures a width of ~ 100 G., centered at the free electron value (for values of g between 2.035 and 1.975). In the case of the arsenic-containing radicals studied here, there appeared to be little interference. The radical cation of triphenylphosphine, however, could not be observed, presumably because its signal was buried by the considerably stronger solvent radical signal.

For this reason, then, it is clear that the photolysis-esr experiment will be best applied to systems likely to produce radicals

exhibiting resonances somewhat removed from g = 2.00. This situation will obtain, of course, in the case where the radical simply resonates at g not close to 2.00. It will also be true where the radical exhibits large hyperfine splitting, so that signals occur at quite high and low fields, while g may actually be quite close to 2.00. It is to be noted that the anisotropy of the g tensor and the deviation from the free-electron value increase going downward in the periodic table.

With this restriction in mind, then, it is proposed to carry out low temperature uv-photolyses of triphenylstibine and triphenylbismuthine in rigid organic glasses. Not many stable organic stibines and bismuthines are known, but these two have been the subject of an electronic spectral study (7). Our work on substituted arsines showed remarkably little variation of esr results with changing substituents on the heteroatom. Both compounds are expected to yield radicals which exhibit hyperfine splitting (8):

^{121}Sb	I = 5/2	natural abundance =	57.25%
^{123}Sb	7/2		42.75
^{209}Bi	9/2		100.0

Because both are below arsenic in the periodic table, the g-values observed should deviate markedly from the free-electron value. It will be of interest to note the ratio of radical cation to divalent neutral species produced in the photolysis. One might expect the stability of the radical cation to decrease going downward in the periodic table. It is hoped that these experiments might help to clarify the meaning of the results already obtained with the arsines.

It is further proposed to photolyze diphenylselenide at low temperature in an attempt to produce the corresponding radical cation. The (R-Se·) species generated in previous studies have been produced by photolysis of diselenide compounds (3). Perhaps by using selenoethers with aryl substituents, radical cations of these molecules can be stabilized and detected, as well as species of the type R-Se. Familiarity with the esr properties of the R-Se species should make interpretation of the results more straightforward. ^{77}Se ($I=\frac{1}{2}$) is 7.58% abundant in the naturally occurring element, and hyperfine satellites are sometimes observed. The g-values observed to date for selenium radicals ($g_{\|}=2.12$, $g_{\perp}=2.08$ for $C_{12}H_{25}Se$)(3) indicate that the products from photolysis of $(C_6H_5)_2Se$ should be well clear of the solvent radical region.

Besides routine esr studies on these new systems, it is clear that more detailed work on the low temperature photolyzed arsines would be of value. It was mentioned in Part I, Chapter 3 that the esr measurements at K-band were attempted but failed due to technical problems. In order to clarify esr interpretations, measurements in systems of this sort should be carried out at the two different microwave frequencies. Measurement of the electronic absorption spectra of these samples should be performed, and also low temperature infrared and Raman studies. These measurements might be of considerable help in identifying and more fully characterizing the species present. The types of studies possible are limited by the necessity to work at low temperature and in rigid media. One final experiment which might be attempted in connection with these is to measure the esr spectrum of a high energy-irradiated (X or γ-rays; electron bombardment) single crystal of triphenylarsine. Considerably

more detailed information is attainable from a single-crystal study than from those carried out on randomly oriented systems (9).

Important applications of this technique for studying unstable paramagnetic species may be found in the field of coordination chemistry. It has recently been used successfully in these laboratories to produce ruthenocenium cation (10), an unstable hydride-phosphine complex of cobalt(II) (11), and thallium-containing radicals (12). Our results with nickel-diarsine complexes indicate that the expected photochemical process need not always occur, however. It does appear that the technique could be applied to a number of problems involving the stabilization and characterization of metal complexes which are unstable under ambient conditions.

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PROPOSITION III

The process of nitrogen-fixation by biological systems must be ranked as one of the most surprising chemical processes known, and at the same time, one of the most essential to life. It has been estimated (1) that every year 100 million tons of nitrogen are fixed by living systems on this planet. That biological nitrogen fixation takes place under normal atmospheric conditions is remarkable, considering the extreme conditions required for the current industrial processes for nitrogen fixation (450°C,250-1000 atm. N_2) (2). A satisfactory solution to the nitrogen-fixation problem could drastically increase the world protein supply and thus buy time in the impending struggle with overpopulation.

Biological nitrogen-fixation was first described in 1838 by Boussingault (2), and since that time has been detected in leguminous and non-leguminous plants and free-living bacteria, both aerobic and anaerobic. In 1956, Carnahan (2-4) first prepared cell-free extracts capable of fixing molecular nitrogen. Since that time, considerable progress has been achieved in describing the nitrogen-fixing system biochemically (2,4,5). In the past few years, a number of inorganic chemists have begun to study the nitrogen-fixation problem from a different vantage point. In 1965, Allen and Senoff (6) reported the first of a rapidly growing class of transition metal complexes with coordinated molecular N_2. In 1964, Vol'pin and Shur (7) first described systems of catalysts based on metal complexes which fix N_2 at room temperature. While progress in the area of inorganic model systems is impressive

(8,9), the systems under study have not yet become economically important, and are still quite different in composition from the biological systems (10).

The isolation and purification of N_2-fixing, cell-free extracts from Azotobacter vinelandii has recently been reported (11). These fractions have been found to contain both iron and molybdenum. Requirements for the reaction are an ATP generator, Mg^{++}, and a reducing agent, for example dithionite ($Na_2S_2O_4$). In some living systems, the reducing agent appears to be pyruvate, and electrons are transported to the nitrogen-fixing enzyme by ferredoxin (12). The N_2-fixation reaction appears to be a two-step process, as evidenced by the fact that if the substrate, molecular N_2, is not provided, but all other requirements are furnished to the enzyme system, evolution of H_2 occurs. The first step is thought to involve activation of the electron donor which functions in the subsequent reduction of N_2 to NH_3 (13). This second step is known as the "nitrogenase" activity. If substrate is not present, the activated electron donor reduces protons to H_2. Hardy and Knight (13) have observed that ATP breakdown accompanies H_2 formation, and have reported that the "reductant-dependent ATPase" and "ATP-dependent H_2 evolution" activities apparently cannot be separated. The role of ATP in the reaction has not been studied in detail, but one function is presumably to increase the reduction potential of the electrons supplied by the reducing agent. Further evidence for the two-step nature of the process is that the nitrogenase activity is inhibited by low concentrations of CO, while the H_2-evolution activity is not. Chelating agents, such as α,α'-dipyridyl and o-phenanthroline, inhibit both activities,

indicating that metal ions do occupy important positions in the active site(s) of the enzyme system.

The isolation of the nitrogenase activity in cell-free systems has allowed much biochemical work to proceed. The level of purification attained is not, however, what one would generally hope to have for detailed physical measurements on the enzyme. While the purification is about 25-fold, some inhomogeneity of the two main protein fractions (both of which appear to be necessary for any type of activity) is observed by ultracentrifugation (11). However, one esr study has been carried out on N_2-fixing particles from Azotobacter vinelandii, and signals were observed at g = 1.94 and 1.97 whose intensity was quite sensitive to the presence of N_2 (14). These signals are known to be characteristic of non-heme iron and molybdenum (V). It is not expected that impurities in the enzyme preparations should interfere with these signals, simply because most impurities will be diamagnetic, and the only paramagnetic impurities which would resonate in this region are non-heme iron and molybdenum(V) impurities, which would exhibit resonances essentially identical to those observed here. Because the highly impure Azotobacter particles gave esr spectra which showed strong N_2-dependence of the intensity, it seems likely that this purified extract should be suitable for more detailed esr measurements than those performed on the Azotobacter particles (14).

The specific roles which the molybdenum and non-heme iron play in the nitrogen-fixing system are not known. The presence of both of these has been reported in a number of enzymes involved in electron transport. Two of these enzymes, xanthine oxidase (15) and aldehyde

oxidase (16), are known to contain both molybdenum and non-heme iron, and have been the subject of quite detailed esr studies. While some of the molybdenum and non-heme iron sites are involved in electron transport in the N_2-fixing system, it appears that there is the added function that one or both of these metal ions binds N_2. It has been found that molecular hydrogen, carbon monoxide, and nitric oxide all exhibit competitive inhibition of N_2-fixation (2). This type of competitive kinetic behavior is taken to mean that these inhibitors compete with substrate for the active site (17). CO is also known to bind to hemocyanin (18), hemoglobin (19), and other metal proteins. In each case it was shown that the "dead-end" inhibition was caused by formation of a stable metal complex blocking the active site. The fact that the nitrogenase extract is effective in reducing a wide variety of simple substrates (N_2O,C_2H_2, N_3^-,HCN,CH_3NC) all of which are good ligands with similar electronic properties is additional evidence for metal-bound N_2. It should be noted that no direct physical evidence has been presented yet for this intermediate, but it does appear that N_2 is bound by either non-heme iron or molybdenum, and that the inhibitors bind at the same active site.

In order to better characterize the metal ion-apoprotein interaction in this enzyme system, and to locate the site of N_2-binding in the active enzyme, certain esr experiments are proposed. First, since the purified components (I and II) prepared by Bulen and Lecomte from the N_2-fixing system of Azotobacter (11) have not been studied by esr, it is proposed to carry out esr measurements on these components under varying conditions. It was reported that I contained only non-heme iron and that II contained both non-heme iron and molybdenum. Careful esr

measurements on proteins similar to II have been carried out (16), and the results of that work should prove very helpful in adjusting conditions (temperature, reductant concentration, substrate concentration, esr modulation power) for the optimum separation of the iron and molybdenum signals in this spectrum. Detailed esr studies on another non-heme iron protein from Azotobacter (20) should likewise be of help in studying I. If such studies appear promising, it is possible to observe ^{95}Mo hyperfine splitting by enriching the sample with ^{95}Mo (15). The magnitude of the Mo hyperfine has been used, with the g-value, in assigning coordinating ligands to the Mo ion (21). In the proteins studied to date, Mo is thought to be bound by sulfur ligands. Enrichment is carried out by simply growing the bacteria in a medium with ^{95}Mo molybdate. A more bizarre procedure was necessary to obtain ^{95}Mo-enriched xanthine oxidase from milk (22).

It is further proposed to measure the esr spectrum of these extracts with $^{15}N_2$ in place of ordinary $^{14}N_2$ and to see whether the molybdenum signal or either of the non-heme iron signals change. This substitution should also be carried out using the various inhibitors known to bind the active site, H_2, D_2, ^{13}CO, and NO, and the esr observed. It should be noted that any of the other substrates could also be used for this purpose. It is expected that the esr signal corresponding to the metal ion which binds N_2 and inhibitor will change when different adducts are formed, if the nuclear spin of the atom bound to the metal changes or there is a dramatic change in the electronic structure of the ligand. This effect has been observed in the molybdenum(V) esr signal of methanol-inactivated aldehyde oxidase (16). It is expected that in this case, a

change in the shape of the esr signal should be observed with different adducts, rather than actual resolution of hyperfine lines. Line broadening was observed for some non-heme iron esr signals on substituting with ^{57}Fe (23) and ^{33}S (20). Careful measurements on these systems under identical conditions will be necessary, but since it will only be necessary to detect a measurable change in the spectrum, it should be possible. If further purification of the proteins is necessary, it should be possible to assay for esr signal to purify so as to maximize that, rather than enzymic activity. While such a procedure may be open to criticism, much detailed esr work is currently done on biological samples which have lost activity in the course of purification procedures (20). It is presumed that the structure of the region of interest of the protein fragment exhibiting the esr signal is not much different from that in the active protein. Certainly any change in the signal with increasing purification is easily monitored.

A current postulated mechanism for nitrogenase reactions is reproduced as Figure 1. This mechanism seems to fit the data now available. What is needed is more detail about the nature of the enzymes and the reactions involved. Attempts to clarify the course of the nitrogen reduction reactions have recently been carried out, using a model system (24). The experiments proposed here can serve to determine the nature of the N_2 binding site. In view of the known deactivating effect of methanol acting on the molybdenum active site in aldehyde oxidase (16), and the fact that CO in low concentrations does not inhibit the action of non-heme iron electron transport proteins, it may be that N_2 is bound by Mo. It is actually difficult to make meaningful speculations without

more experimental evidence concerning the structure of the protein. It is hoped that the study proposed above will help provide such information.

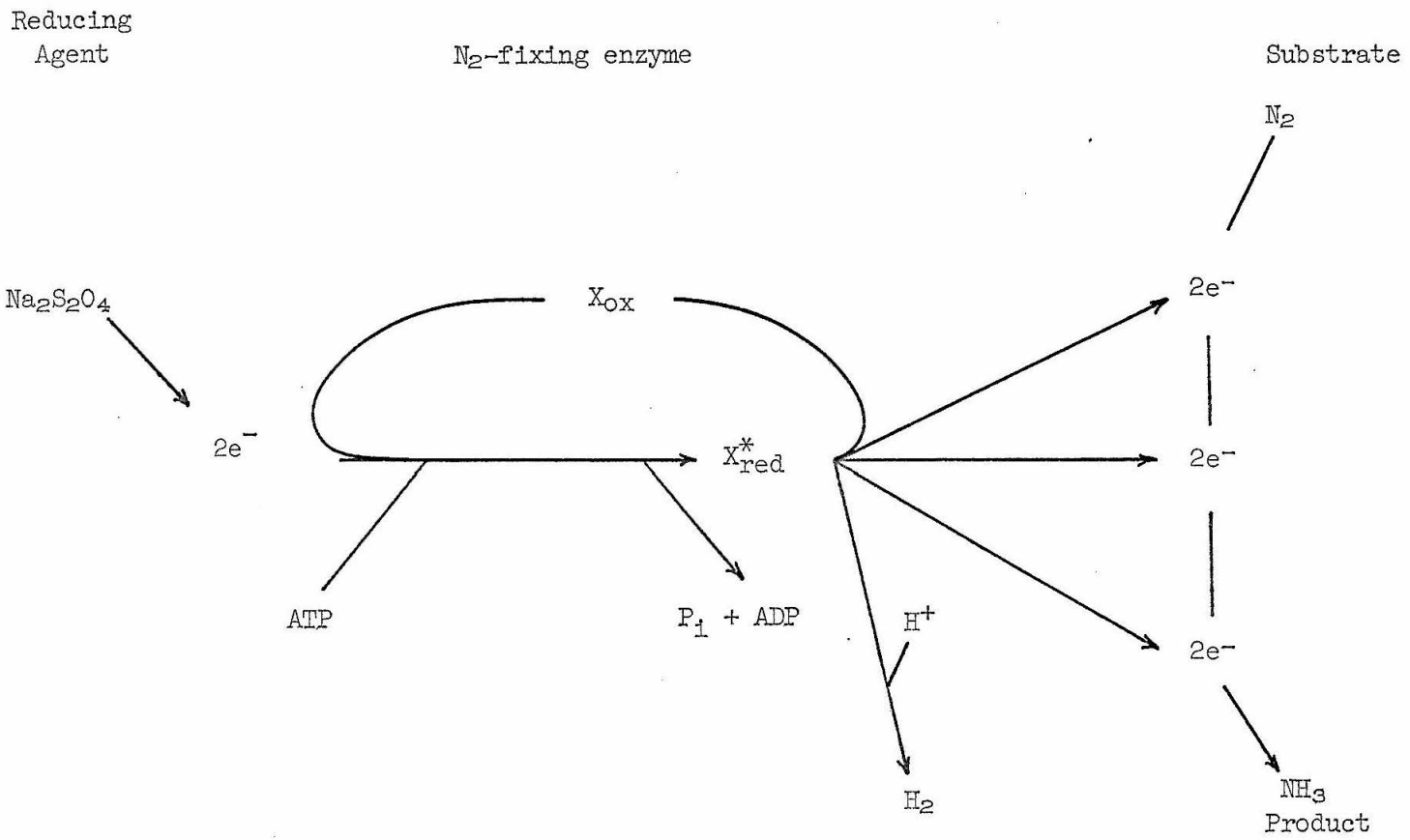

Figure 1. A current postulated mechanism for nitrogen-fixation (from Ref. 2).

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PROPOSITION IV

Since the original preparation (1) of the very unusual complex of diarsine with nickel in the formal oxidation of +3, $Ni(diars)_2X_3$(X=Cl,Br,CNS), it has been the subject of a number of electronic and molecular structural studies (2-5). Nyholm has reported the preparation and characterization of bis-diarsine complexes of nickel in the formal oxidation states of +2, +3, and +4 (1,6), and has described the conditions necessary to interconvert these species. While rather severe conditions (15N. HNO_3) are necessary to produce the formally nickel(IV) complex, $[Ni(diars)_2Cl_2](ClO_4)_2$, the two less highly oxidized species are fairly easily interconverted. For example, oxidation of $Ni(diars)_2Cl_2$ is accomplished by simply refluxing in ethanol containing HCl (1 M.) with air bubbling through the solution for two days (1). Reduction of the product of this reaction, $Ni(diars)_2Cl_3$, is easily accomplished by treating the solution with sulfur dioxide.

A crystal structure determination (3) has shown $Ni(diars)_2Cl_3$ to be six-coordinate in the solid, with trans-chlorides. Conductivity measurements ($c \approx 10^{-3}$ M.) and a potentiometric titration with silver ion indicate that the six-coordinate form is maintained in solution (1). Also, the visible absorption spectrum appears to be the same in the solid and solution (4). There is now a large body of evidence that the divalent complexes of the form $M(diars)_2X_2$ (M=Ni,Pd,Pt;X=Cl,Br,I,CNS,NO_2,tu, CN) are five-coordinate in organic solvents (7-9). While the oxidation of $Ni(diars)_2Cl^+$ has been shown to occur readily in the presence of

excess chloride, in the absence of chloride, the oxidation will not proceed. The four-coordinate $Ni(diars)_2(ClO_4)_2$ (7) has not been oxidized to form any stable species, and no five-coordinate, oxidized complex has been isolated. It is apparent that the axial field provided by the anionic ligands is in some way necessary to stabilize the oxidized bis-diarsine nickel unit.

The reduced species, $Ni(diars)_2X^+$, is five-coordinate, then, while the oxidized species, $Ni(diars)_2X_2^+$, is six-coordinate. Since neither $Ni(diars)_2X_2^0$ or $Ni(diars)_2X^{2+}$ have ever been detected, it is not obvious what the reaction mechanism for the redox process should be. A number of kinetic experiments are proposed to determine the mechanism of the oxidation and reduction reactions.

Nyholm (1) has reported a potentiometric titration of $Ni(diars)_2Cl_2$ with cerium(IV) sulfate as oxidant. It would be possible to use cerium(IV), hydrogen peroxide, or a number of other oxidizing agents to study the oxidation of $Ni(diars)_2Cl^+$. Nyholm reports E^o = +0.77 v. for the process. For the reduction of $Ni(diars)_2X_2^+$, sulfur dioxide has been used, and sodium sulfite in dilute acidic media would quite likely be a suitable substitute. In aqueous solution, the reduced species $Ni(diars)_2X^+$ slowly loses diarsine by hydrolyses. Nyholm (1) has circumvented this problem by carrying out the potentiometric titration at 0°C. Alternatively, methanol, which does not attack $Ni(diars)_2X^+$, could be used as solvent. Using methanol as solvent, a weak oxidant, such as H_2O_2 or O_2 and acid, should be used. The use of non-absorbing oxidizing and reducing agents makes it possible to follow the reaction spectrophotometrically. This reaction has been observed

unintentionally in the course of making electronic spectral measurements on the five-coordinate species (9). Traces of peroxides in 2-methyltetrahydrofuran, one component of solvent mixtures used in that work, cause slow oxidation of $Ni(diars)_2X^+$ to $Ni(diars)_2X_2^+$. Because the spectra of $Ni(diars)_2X^+$ and $Ni(diars)_2X_2^+$ show equal extinction coefficients for two or three values of λ, the presence or absence of isosbestic points in the electronic spectra of solutions undergoing these reactions is a test for the absence or presence of absorbing intermediates. This technique has been used by Peloso et al. (10) to demonstrate the existence of the intermediate species $Co(diars)_2(CNS)Cl^+$ in the substitution reaction of $Co(diars)_2Cl_2^+$ with NCS^-. This technique could also be used in this case to test for absorbing intermediates.

Before going to the redox reactions, it may be of help to examine the possible ligand substitution processes. Those which will be relevant to the redox reactions are

$$Ni(diars)_2X^+ + Y^- \rightleftharpoons Ni(diars)_2Y^+ + X^- \qquad (1)$$

and

$$Ni(diars)_2X_2^+ + Y^- \rightleftharpoons Ni(diars)_2XY^+ + X^- \qquad (2)$$

The rate of (1) was crudely estimated using nmr methods (9), with the result Rate $k \gtrsim 10^4$ sec.$^{-1}$ (300°K). It is not known whether the reaction is associative or dissociative. It is proposed to carry out temperature-jump kinetic measurements (11) as a function of reactant concentration to determine the associative or dissociative nature of (1). An associative process would indicate the presence of a six-coordinate intermediate or activated complex, with a maximum half-life of $\sim 10^{-4}$ sec. The visible

absorption spectra of the different five-coordinate complexes of this series are known and can be used to follow the reaction in the T-jump experiment.

Reaction (2) is analogous to the ligand substitution process for the corresponding cobalt(III) complex. The dissociative rate constant for $^{36}Cl^-$ substitution into $Co(diars)_2Cl_2^+$ was found to be $k_1 = 5 \times 10^{-6}$ sec.$^{-1}$ (10). It is quite unlikely that the nickel complex will undergo substitution so slowly, but the mechanism is expected to be dissociative,

$$Ni(diars)_2Cl_2^+ \xrightarrow{\text{slow}} Ni(diars)_2Cl^{2+} + Cl^- \xrightarrow[+\ {}^*Cl^-]{\text{fast}} Ni(diars)_2Cl{}^*Cl^+ \quad (3)$$

If sufficiently slow, the reaction can be studied by radioactive exchange. Otherwise, study of this reaction will be difficult, due to the similarity in absorption spectra of the different $Ni(diars)_2X_2^+$. If the spectra could be sorted out, a T-jump study would be of value.

For the reduction reaction, possible mechanisms are listed below, along with the corresponding rate expressions.

$$Ni(diars)_2X_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(diars)_2X^{2+} + X^- \xrightarrow[k_2]{+Red} Ni(diars)_2X^+ + Ox \quad (4)$$

Applying the steady-state approximation to $Ni(diars)_2X^{2+}$,

$$\text{Rate} = \frac{k_1k_2(S)(Red)}{k_{-1}(X^-) + k_2(Red)} \quad \text{where } S = Ni(diars)_2X_2^+$$

Comparing the substitution rate determined above with the rate of oxidation should permit one to say which of the two steps is rate-determining. For a slow first step, the rate expression reduces to

$$\text{Rate} = k_1(S) \ .$$

For a rapid first step, it becomes

$$\text{Rate} = \frac{k_1 k_2}{k_{-1}} \frac{(S)\ (\text{Red})}{(X^-)} \ .$$

$$Ni(diars)_2X_2^+ + \text{Red} \xrightarrow{k} Ni(diars)_2X^+ + X^- + \text{Ox} \qquad (5)$$

$$\text{Rate} = k(S)(\text{Red})$$

$$Ni(diars)_2X_2^+ + \text{Red} \xrightarrow{k_1} Ni(diars)_2X_2^{\,o} \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} Ni(diars)_2X^+ + X^- \qquad (6)$$

$$+$$

$$\text{Ox}$$

$$\text{Rate} = k(S)(\text{Red})$$

Determination of the rate law for the reduction will distinguish mechanism (4) from (5) and (6), but will not distinguish (5) from (6). This ambiguity can not be removed by standard kinetic methods. However, in view of the known substitution-lability of the $Ni(diars)_2X^+$ complexes (9), it seems unlikely that $Ni(diars)_2X_2^{\,o}$ will be a long-lived species. If the mechanism of the five-coordinate X-exchange reaction described above is associative, then the half-life of the six-coordinate species must be $\lesssim 10^{-4}$ sec.

Turning to the oxidation reaction, the following possible mechanisms should be considered:

$$Ni(diars)_2X^+ + \text{Ox}' \xrightarrow{k_1} Ni(diars)_2X^{2+} + \text{Red}' \underset{-X^-}{\overset{+X^-}{\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}}} Ni(diars)_2X_2^+ \qquad (7)$$

In octahedral substitution reactions, the second step in (7) is rapid. This was observed in the case of $Co(diars)_2Cl_2^+$ (10). In that case,

we have

$$\text{Rate} = k_1(S)(Ox')$$

$$Ni(diars)_2X^+ + X^- + Ox' \xrightarrow{k} Ni(diars)_2X_2^+ + Red' \qquad (8)$$

$$\text{Rate} = k(S)(Ox')(X^-)$$

$$Ni(diars)_2X^+ + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(diars)_2X_2^{\,o} \xrightarrow[k_2]{+Ox'} Ni(diars)_2X_2^+ + Red' \qquad (9)$$

$$\text{Rate} = \frac{k_1k_2}{k_{-1}}(S)(Ox')(X^-)$$

It should be noted that (8) and (9) display the classic mechanistic ambiguity of rate law determinations. Ordinary kinetic measurements can not distinguish between sets of reactants in equilibrium with one another. If Rate $\lesssim 10^3$ sec.$^{-1}$ M.$^{-1}$ in (9), this ambiguity could be removed by carrying out a pre-steady state kinetic measurement by the stopped-flow technique (12). As has been noted earlier, it is likely that this reaction is above this rate limit.

There is one piece of evidence not yet mentioned which may bear on the question of intermediate species. This is that $Ni(diars)_2Cl^+$ in a rigid glass at 95°K is not photooxidized, while $Ni(diars)_2Cl_2^+$ <u>is</u> photoreduced (9). This is taken to be evidence against the intermediate $Ni(diars)_2Cl^{2+}$. Because the bonding in $Ni(diars)_2X_2^+$ is not well understood, it is not profitable to speculate on factors affecting the stability of $Ni(diars)_2X^{2+}$. Both a simple crystal field description and the "stable octet" rule predict that $Ni(diars)_2X^+$ should be more stable than $Ni(diars)_2X_2^{\,o}$. However, $Ni(diars)_2I_2$ has been shown to be six-coordinate with covalent bond distances in the solid (13).

It is perhaps worth noting that while the structure of the

paramagnetic thiocyanate complex [$Ni(diars)_2(CNS)_2^+$] has not been studied, the existence of two isomers of $Ni(diars)_2CNS^+$ (19) could complicate the kinetic picture considerably, due to the possible necessity to isomerize the thiocyanate ligand at some point.

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PROPOSITION V

Current theories about the origin of life on Earth from simple molecules are based on the description first given by the Russian scientist Oparin (1). This description is based on the current understanding of the nature of pre-biotic conditions on Earth: the components of the atmosphere and geosphere, and the energy sources available.

Oparin's description, as modified by Urey (2,3) is presented here. About 4.5 billion years ago, the earth was condensed from a low-temperature cosmic cloud (4), and since that time, temperatures have remained rather close to present temperatures (3). The atmosphere was reducing in character, with CH_4, N_2, NH_3, H_2O, and H_2 as the primary components. Much of the earth was covered by water. Under these conditions, the action of electrical discharge (lightning) and ultraviolet radiation from the sun produced some larger molecules, most of which were in turn decomposed by radiation from the sun. Some of these larger molecules were not decomposed, however, and passed into the oceans, where further reactions occurred, leading to more and more complex molecules. After some millions of years the oceans resembled a thin, organic "soup," and eventually, by chance, the first viable self-replicating macromolecule was formed. The oldest known algal fossil has been dated as 2.7 billion years old (5), so the complete process, as described, must have occurred in less than 2 billion years. Towards the end of this time, the atmosphere changed from reducing to oxidizing, as a result of the escape of H_2 from the atmosphere. This oxidizing

atmosphere is of course known to exist presently.

Acting on a suggestion of Urey (2), in 1953 Miller (6) demonstrated the production of simple α-amino acids under primitive earth conditions. His experiment was simply to pass an electric discharge through a gaseous mixture of CH_4, NH_3, H_2, and H_2O vapor for a period of one week. Major products were formic acid, glycine, alanine, lactic acid, and glycolic acid. Since the initial work of Miller, many other workers have achieved success in the synthesis of biologically important monomers under supposed pre-biotic earth conditions, using a variety of energy sources. Nearly all of the important α-amino acids (7), a large number of assorted aldehydes, ketones, polyhydroxy compounds, and even some purine and pyrimidine bases (8-10) have been prepared under relatively mild conditions. Some initial progress in forming polynucleotides and polypeptides from the monomers has been achieved (11,12).

One important problem involved in the chemical synthesis of life as it must have occurred is that the solubility of phosphate in sea water is very low (0.125 ppm) compared to the concentrations known to exist in living cells (herbaceous leaves, 250-750 ppm; human blood plasma, 30-60 ppm) (13). Phosphate is of course an essential component in DNA and RNA, and phosphorylation reactions are a primary means of energy transport in cells (ATP → ADP + P_i, etc.). Synthetic reactions involving phosphate are expected to be difficult with such low concentrations of free phosphate. Success in carrying out phosphorylation reactions of nucleosides has been achieved by Orgel (14) using reasonable conditions with the exception of quite high phosphate concentration (1 M.).

An interesting approach to the phosphate concentration problem was provided by Miller (15), who was able to synthesize pyrophosphate in 27% yield by shaking a suspension of the common phosphate mineral, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, with potassium cyanate (10^{-3} M.) for 35 days at 20°C. Calvin (16), following up earlier work of Akabori (17), used powdered kaolinite $Al_4(Si_4O_{10})(OH)_8$ to promote the dicyanidiamide (DCDA)-directed condensation of phosphate to pyrophosphate and ADP to ATP. He noted that the key to the catalytic effect of kaolinite is probably its known ability to substitute OH^- ions with $H_2PO_4^-$ ions (18).

It is proposed to study phosphorylation reactions in some detail, using conditions approximating those on pre-biotic Earth. It appears that the heterogeneous systems used by Akabori, Miller, and Calvin may provide a way of circumventing the phosphate concentration problem. However, their work is in the nature of preliminary reports, and a number of fairly important questions remain unanswered. One problem with studies such as these is that so many variables are involved that it is difficult to make meaningful comparisons between the different studies. This work has characterized the important variables involved, however. These are substrate, condensing agent, temperature, source of phosphate, and divalent metal ion.

One factor in the phosphorylation reaction which deserves further study is the role of the divalent metal ion. Miller (15) speculates that calcium ion in hydroxyapatite probably complexes phosphate in the course of the condensation of phosphate to pyrophosphate. Orgel (14), however, indicates that adding various divalent metal ions does

not promote nucleotide formation when HCN is used as condensing agent. It is well known (19) that Mg^{2+} (Mn^{2+}, Ca^{2+}, or Co^{2+} can substitute) is an obligatory cofactor for the kinases, enzymes which direct the phosphorylation of simple sugars and nucleosides. Complexes of ATP with various metal ions, including Ca^{++} and Mg^{++} are known (20). In view of this, it does appear likely that divalent metal ions could have played an important role in pre-biotic phosphorylations. The effect of dissolved divalent metal ions on phosphorylation should be tested for comparison with the results obtained on heterogeneous systems involving the same divalent ions. Also, the same system should be used to compare the relative effects of apatite, which contains a divalent cation, with kaolinite, which does not, in promoting phosphorylation. Various condensing agents, cyanate, cyanamide, DCDA, cyanogen, thioformate, cyanoformamide should be tested in conjunction with the heterogeneous systems to see which yield the best results. Certainly the simplest reaction to study would be the condensation of phosphate to pyrophosphate described by Miller (15). It would then be worthwhile to examine the phosphorylation of a simple sugar, using the conditions developed in the pyrophosphate study. This reaction has apparently not been carried out under primitive earth conditions, and is somewhat simpler than the nucleoside → nucleotide conversion.

One final problem associated with phosphorylation reactions under pre-biotic earth conditions has been pointed out by Orgel (21). He found that heating inorganic phosphate in the presence of uridine did lead to production of some uridine phosphates (65°C, 6 months). However, subjecting uridine phosphates to the same conditions led to

extensive dephosphorylation. Unfortunately, phosphate concentrations used were not reported in this study. It is possible that using a relatively insoluble phosphate mineral, such as hydroxyapatite for the reaction may eliminate this dephosphorylation problem, since it avoids high phosphate concentrations. At any rate, the effect of the reaction conditions on the products over extended periods of time should be tested in the heterogeneous phosphorylation systems proposed here for study.

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